

VIA ELECTRONIC MAIL, AND U.S. MAIL

April 25, 2007

SR-6J

Mr. Jerry C. Winslow Principal Environmental Engineer Xcel Energy 414 Nicollet Mall (Ren. Sq. 8) Minneapolis, Minnesota 55401

RE: Final revisions to the Remedial Action Objectives
Ashland/NSP Lakefront Superfund Site

Dear Mr. Winslow:

In accordance with the Administrative Order on Consent (AOC), CERCLA Docket No. V-W-04-C-764, Section X, Subparagraph 21(c), the United States Environmental Protection Agency (EPA) is modifying the Remedial Investigation Report (RI), Appendix A, Remedial Action Objectives Technical Memorandum (RAO) submission to cure certain deficiencies. Within 21 days of the receipt of this letter, the appropriate revisions (attached to this letter) to Appendix A, Remedial Action Objectives Technical Memorandum should be made and submitted to EPA. By letter dated December 22, 2006, EPA previously provided Xcel Energy a notice of deficiency regarding the RI. By this letter EPA is providing further notice of deficiency and giving Xcel Energy 21 days to cure the deficiency by incorporating the modifications as shown in the attached RAO document.

In addition, EPA is attaching a Technical Memorandum discussing the Sediment Preliminary Remediation Goal (PRG) for the Ashland/NSP Lakefront site. EPA modified sections of the RAO Technical Memorandum based on the PRG contained herein.

If you have any questions or would like to discuss things further, please contact me at (312) 886-1999.

Sincerely,

Scott K. Hansen Remedial Project Manager

cc: Dave Trainor, Newfields
Jamie Dunn, WDNR
Omprakash Patel, Weston
Henry Nehls-Lowe, DHFS
Ervin Soulier, Bad River Band of the Lake Superior Chippewa
Melonee Montano, Red Cliff Band of the Lake Superior Chippewa

bcc:

File, SR-6J Craig Melodia, C-14J

Scott Hansen /R5/USEPA/US

09/27/2007 11:24 AM

Subject Fw: Tech. Memo. on PRGs for sediment

---- Forwarded by Scott Hansen/R5/USEPA/US on 09/27/2007 11:24 AM -----

Scott Hansen /R5/USEPA/US

To

To

04/25/2007 04:15 PM

Subject RE: Tech. Memo. on PRGs for sediment

Jerry,

Here is the Technical Memorandum establishing the PRGs for the sediment at the Ashland site. This will also change the RAO document which also will be sent today. So, please make the changes to all the documents that report the PRG is 53 ppm TPAH at 1% OC dwt for sediments.

As for the schedule, EPA approves the two week extension to submit the revised Alternative Screening Tech Memo. That means the revised Tech memo will be due on May 9th.

If you have any questions or would like to discuss it further please give me a call.

Scott

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APPENDIX A REMEDIAL ACTION OBJECTIVES TECHNICAL MEMORANDUM

In accordance with the AOC, this Remedial Action Objectives Technical Memorandum was prepared to document objectives based upon human health and ecological risk assessment results. This document primarily focuses on the chemicals of potential concern (COPCs) for each media, potential exposure pathways and receptors, and acceptable contaminant levels, or range of levels (protectiveness), at particular locations for each exposure route. A brief summary of the Ashland Lakefront Site is provided along with an outline of the remedial alternatives process

A.1. INTRODUCTION

The Site contains property owned by NSPW, a portion of Kreher Park, the former Wastewater Treatment Plant (WWTP), and a portion of the Chequamegon Bay inlet area adjacent to Kreher Park. The primary contaminant source is the former manufactured gas plant which previously occupied the NSPW property, In addition, other possible industrial operations might have contributed to the contaminant source at Kreher Park.

Site characterization began in 1989 when apparent contamination was discovered at Kreher Park. The primary contaminants at the Site are derived from tar compounds, including volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs). Soils, groundwater, and offshore sediments have been impacted. Additionally, free-product derived from the tars is present as a non-aqueous phase liquid (NAPL) in the upper reaches of a filled ravine on the NSPW property, at isolated areas at Kreher Park including the former "seep" area, in the offshore sediments, and in the upper elevations of the deep Copper Falls aquifer. The free-product in the deep aquifer is surrounded by a dissolved phase contaminant plume that extends north from the area of the free-product in the direction of groundwater flow. Although contaminants have migrated down gradient in the underlying Copper Falls aquifer, both the vertical and lateral extent of contamination is limited by strong upward gradients that create artesian conditions at the Lakefront.

NSPW implemented interim removal actions in 2000 to mitigate exposure risks to contaminants and to recover free-product from the deep aquifer. A low-flow pumping system currently extracts free-product from the deep aquifer, treating the entrained groundwater before discharging it to the City of Ashland's sanitary sewer. Additionally, NSPW installed an extraction well at the base of the filled ravine that was the source of the seep discharge at Kreher Park. This extraction well was part of a larger interim action that included excavation of contaminated materials at the former seep area and placement of a low-permeability cap to eliminate the intermittent seep discharge and mitigate environmental exposure of the associated contaminants.

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This Remedial Action Objectives Technical Memorandum is the first of three submittals to identify the need for corrective action, and, develop and screen remedial options in accordance with the November 2003 AOC. Subsequent documents will screen appropriate technologies. Treatability studies may also be conducted. A Detailed Analysis of Alternatives (Feasibility Study) will be prepared as the final submittal of these documents.

A.2 CHEMICALS OF POTENTIAL CONCERN

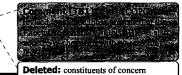
Fluorene

Indeno(1,2,3-cd)pyrene

The primary contaminants at the NSPW Site consist of VOCs and semi-volatile organic compounds (SVOCs). Benzene is the most commonly occurring VOC. SVOCs consist predominantly of a group of PAH compounds. The most commonly occurring PAH at the Site is naphthalene. Some metals (lead, thallium, and arsenic) and inorganic compounds (cyanides) have also been found, but these are sporadic are not considered significant COPCs.

The baseline revised Human Health Risk Assessment (HHRA) (URS, 2007) used a tiered, riskbased approach to evaluate COPCs for the various exposure scenarios. The results of the HHRA evaluation found the following <u>COPCs</u> for the Site.

List of COPCs Identified by the HHRA



Benzo(a)anthracenc	1-Methylnaphthalene	Antimony	1-Methylnaphthalene	1-Methylnaphthalene	1.2,4- Trimethylbenzene
Benzo(a)pyrene	2-Methylnaphthalene	<u>Iron</u>	2-Methylnaphthalene	Benzo(a)anthracene	1,4- Dichlorobenzene
Benzo(b)fluoranthene	Acenaphthene	Manganese	Acenaphthene	Benzo(a)pyrene	Benzene
Benzo(k)fluoranthene	Benzo(a)anthracene	<u>Vanadium</u>	Benzo(a)anthracene	Benzo(e)pyrene	Carbon tetrachloride
Chrysene	Benzo(a)pyrene	1-Methylnaphthalene	Benzo(a)pyrene	Benzo(b)fluoranthene	Trichloroethylene
Dibenzo(a,h)anthracer	e Benzo(b)fluoranthene	2-Methylnaphthalene	Benzo(b)fluoranthene	Dibenzo(a,h)anthracene	
Indeno(1,2,3-cd)pyren	Benzo(k)fluoranthene	Benzo(a)anthracene	Benzo(k)fluoranthene	<u>Dibenzofuran</u>	
	Chrysene	Benzo(a)pyrene	Chrysene		
	Dibenzo(a,h)anthracene	Benzo(b)fluoranthene	Dibenzo(a,h)anthracene		
	Dibenzofuran	Benzo(k)fluoranthene	Dibenzofuran		
	Fluoranthene	Indeno(1,2,3- cd)pyrene	Fluoranthene		

<u>Fluorene</u>

Indeno(1,2,3-cd)pyrene

Naphthalene

Naphthalene	<u>Naphthalene</u>
 Phenanthrene	<u>Phonanthrene</u>
<u>Pyrene</u>	Pyrene
1,2,4-Trichlorobenzene	1,2,4-Trichlorobenzene
1.2.4-	1.2.4-
Trimethylbenzene	Trimethylbenzene
1.3,5-	1,3.5-
Trimethylbenzene	Trimethylbenzene
<u>Benzene</u>	Benzene
Ethylbenzene	Ethylbenzene
Toluene	Toluene
Total Xylenes	n-Butylbenzene
	sec-Butylbenzene
	Total Xylenes
	Arsenic
	Lead
	Thallium

In the HHRA, the toxicity assessment provides a framework for characterizing the relationship between the magnitude of exposure to a chemical and the nature and likelihood of adverse health effects that may result from such exposure. Chemical toxicity is typically divided into two categories: carcinogenic and noncarcinogenic. Potential health effects are evaluated separately for these two categories, because their toxicity criteria are based on different mechanistic assumptions and associated risks are expressed in different units. Thus, the COPC list was refined using toxicology, pathways, and exposure during the HHRA for the Site. No COPCs were identified in the HHRA for groundwater because groundwater is not used as a potable water supply, though construction worker exposure to groundwater is possible. At the former Waste Water Treatment Plant (WWTP), trespassers who enter the buildings can potentially inhale vapors and have direct dermal contact with contaminated groundwater and NAPLs that have infiltrated the flooded lower level of the facility. The COPCs identified for surface water include PAHs. The COPCs identified for sediment include metals and PAHs. PAHs were found to be COPCs in fish. Several volatile compounds were COPCs in indoor air.

The Baseline Ecological Risk Assessment (BERA) (URS, 2006) evaluated data for all media, including all historical data, to screen and select COPCs from an ecological perspective. Screening was conducted for the various media using appropriate benchmarks. The results of the

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List of COPCs Identified by the BERA

Karista (c.	- Liftigh	4.77 (1.78 (
None	Total PAHe	Total DAHe
	Dibenzofuran	Benzene
1	m-Cresol	Antimonv
	n-Cresol	Barium
	n-Cresol	Cadminm
	1 2 4-Trimethvlhenzene	Chromium
	1 3 5-Trimethylhenzene	Conner
	Renzene	Lead
	Ethylhenzene	Manganese
	Toluene	Mercury
	Total Xvlenes	Selenium
	Antimonv	Silver
	Arsenic	Thallium*
	Barium	Zinc
	Cadmium	Cvanide
	Conner	
	Iron	
	Lead	
	Manganese	
	Mercurv	
	Nickel	
	Selenium	
1	Silver	
	Thallium	
	Vanadium	
	Zinc	
	Cvanide*	

In the BERA, the COPCs were evaluated based on concentrations, pathways, receptors, and likely effects. PAHs were the primary COPC addressed in the BERA.

A.3 POTENTIAL EXPOSURE PATHWAYS AND RECEPTORS

The exposure pathway links the sources, types of environmental releases, and environmental fate with receptor locations and activity patterns. Generally, an exposure pathway is considered complete if it consists of the following four elements:

- A source and mechanism of release;
- A transport medium;
- An exposure point (i.e., point of potential contact with an impacted medium); and
- An exposure route (e.g., ingestion) at the exposure point.

Release mechanisms and transport pathways were evaluated for the Site. Listed below are potential cross-media transfer mechanisms of chemicals:

- Chemicals in subsurface soil may enter groundwater through infiltration/percolation;
- Chemicals in surface soil may be transported to surface water and sediments through surface runoff and backfilling;
- Chemicals in groundwater may be transported to surface water and sediments through groundwater discharge;
- Chemicals in groundwater may be infiltrating the lower level of the former WWTP-located in Kreher Park;
- Chemicals in surface soil may be transported to the atmosphere via volatilization or fugitive dust emission;
- Chemicals in soil or groundwater may be transported to the atmosphere or indoor air through volatilization;
- Chemicals in surface water and sediments may be transported to the tissues of aquatic organisms or higher trophic levels through bioaccumulation; and
- Chemicals in sediments may be released to surface water when sediments are disturbed.

A.3.1 Human Health Receptors and Exposure Scenario

Presented below is an overview of exposure pathways of potential concern selected for further evaluation in the HHRA. Potential receptors are discussed based on medium of interest (i.e., soil, groundwater, sediment, surface water, biota, and air). Updates to the receptor populations identified in the Final Work Plan (URS, 2005) are discussed as necessary.

A.3.1.1 Exposure to COPCs in Soil

Residential Land Use Scenario: Child and Adult Residents

Upper Bluff - There is a residential area located upgradient from the Kreher Park area of the Site at the upper bluff area northeast of the former ravine. Described below were three exposure scenarios assumed in the HHRA for the residential receptors:

Exposure to surface (0-1 ft) and subsurface soil (1-10 feet bgs).

This assumption was made because new construction would involve excavation of soil for the construction of footings or basements. Therefore, subsurface soil would be brought to the surface resulting in a potential exposure pathway for residential receptors. This scenario

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represents the worst case for residential receptors, but is not likely to be the actual scenario associated with the Site.

Exposure to surface soil.

The residential neighborhoods adjacent to the Site are established neighborhoods and are expected to remain so in the future. According to the Ashland Wisconsin Waterfront Development Plan, the future use of the Kreher Park portion of the Site does not include a residential scenario. In an established residential setting and without intrusive activities, receptors would most likely be exposed to surface soil.

Exposure to soil in 0-3 ft bgs.

For informational purposes, COPCs in soil between 0 and 3 ft bgs were also considered for residential receptors based on the assumption that receptors could potentially be exposed to soil from 0-3 ft bgs when performing landscaping or gardening activities.

For the purpose of the HHRA, child and adult residents were assumed to be exposed to COPCs in soil via incidental ingestion, inhalation (of soil-borne vapor and particulates) and dermal contact pathways.

Recreational Use Scenario: Child, Adolescent and Adult Visitors

Kreher Park is now zoned as City parkland. Child, adolescent and adult visitors are assumed to be exposed to COPCs in surface soil via incidental ingestion, inhalation (of soil-borne vapor and particulates) and dermal contact pathways.

Industrial/Commercial Land Use Scenario: Maintenance Workers

Although the final Work Plan indicated maintenance workers currently access the Site, additional information collected during the RI indicates that City workers and utility maintenance personnel do not access the Site. However, the City may develop the existing marina and expand it into the affected area for recreational use. Therefore, a potential future maintenance worker was considered a receptor to surface soil at Kreher Park and the unpaved portions of the Upper Bluff area. It is conservatively assumed that maintenance workers may be exposed to COPCs in surface soil via incidental ingestion, inhalation (of soil-borne vapor and particulates) and dermal contact pathways.

Industrial/Commercial Land Use Scenario: General Industrial Workers

Except for the NSPW facility, no other industrial/commercial facilities exist within the Site. For this HHRA, general workers are defined as NSPW employees involved with non-intrusive, operational activities. Current and potential future general workers are not likely to be subject to significant exposure to environmental media in the normal course of their daily work. Although

the potential for exposure to occur is expected to be low, general workers are assumed to be exposed to COPCs in surface soil via incidental ingestion, inhalation (of soil-borne vapor and particulates) and dermal contact pathways.

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Industrial/Commercial Land Use Scenario: Construction Workers

Upper Bluff and Kreher Park - It is conservatively assumed that construction activities could take place at every area included in this evaluation and it is possible for construction workers to be exposed to COPCs in surface and subsurface soil via incidental ingestion, inhalation (of soilborne vapor and particulates) and dermal contact pathways. For this HHRA subsurface soil is defined as a depth of 10 feet or less, which is a conservative estimate of the limit to which construction activities may occur based on the current and proposed future land use at the Site.

A.3.1.2 Exposure to COPCs in Indoor Air – Residents and Industrial Workers

Upper Bluff - The residential area located upgradient from Kreher Park at the upper bluff area northeast of the former ravine was evaluated. For the purpose of the HHRA, child and adult residents were assumed to be potentially exposed to COPCs volatilizing from soil and groundwater and entering the residences located near the ravine. In addition, potential exposures to COPCs in indoor air were also evaluated for industrial workers who may enter the NSPW service center/vehicle maintenance building periodically.

Kreher Park - trespassers who enter the former WWTP can potentially inhale vapors released by contaminated groundwater and NAPLs that have infiltrated the flooded lower level of the facility. The potential health risks associated with this exposure pathway was part of the RI/FS workplan (URS 2005), but was not evaluated by the HHRA and is a data gap. Despite this shortcoming direct contact exposures to NAPL or "free-product" in groundwater may pose an unacceptable health risk.

A.3.1.3 Exposure to COPCs in Groundwater: Trespassing Land Use Scenario

The final Work Plan indicated that groundwater in the seep area was a potential exposure point for trespassers. However, this exposure point was eliminated because the seep area was capped as part of the 2002 interim action response (URS, 2002). This exposure pathway is no longer complete and was not quantitatively evaluated in the HHRA.

Another potential point of exposure to groundwater is the former WWTP building where groundwater has infiltrated into the basement. The building is locked and the perimeter is fenced with warning signs posted. A quantitative evaluation for the potential trespasser exposures to the indoor air and water inside the former WWTP building was not performed due to the lack of

Industrial/Commercial Land Use Scenario: Construction Workers

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Kreher Park - It is conservatively assumed that construction activities could take place at every area included in this evaluation and it is possible for construction workers to be exposed to COPCs in shallow groundwater at Kreher Park via incidental ingestion, inhalation of vapors, and dermal contact pathways. For this HHRA shallow groundwater is defined as a depth of 10 feet or less, which is a conservative estimate of the limit to which construction activities may occur based on the current and proposed future land use at the Site.

Residential and Industrial/Commercial Land Use Scenarios

Groundwater is present in both the water table aquifer and a confined deep aquifer. Currently the shallow groundwater is not used as a potable water source. There are two artesian wells in the Site vicinity—one located near Prentice Avenue on the eastern boundary of the Site and the other located near the marina on the western boundary. Both wells draw water from the Copper Falls aquifer, the confined deep aquifer that is separated from the shallow groundwater by the Miller Creek Formation (URS, 2005; ATSDR, 2003). The City of Ashland restricted public access to these wells for public use in August 2004. To date water from these wells have met all federal and state safe drinking water standards. Water from these artesian wells is considered safe to drink as Site-related chemicals have not been detected in these wells at levels of concern (ATSDR, 2003).

Except for the two artesian wells, the Copper Falls aquifer is not used for drinking water and is not considered a source of human exposure. Shallow groundwater at the Site is not a drinking water source for the City of Ashland. Drinking water at the Site is provided by the City of Ashland that draws its water from intakes in Lake Superior, located approximately one mile northeast of the Site outside the known extent of surface water contamination. Therefore, there are no known receptors to shallow groundwater beneath the Site.

A.3.1.4 Exposure to COPCs in Surface Water and Sediments

Recreational Use Scenario: Child, Adolescent and Adult Visitors to Kreher Park and Chequamegon Bay

The Site is surrounded by facilities that draw the public to the lakefront – a City marina, public swimming beach, a boat ramp and an RV park and campground. Child, adolescent and adult visitors are assumed to be exposed to COPCs in surface water and sediments via incidental ingestion, inhalation of vapors, and dermal contact pathways while swimming, wading, fishing, or boating. However, only risks associated with swimming and wading activities were quantified in the HHRA. This is because they represent activities that have the greatest contact with impacted media and are considered more conservative than exposures associated with

A.3.1.5 Exposure to COPCs in Fish Tissue

Subsistence fishers were selected as the fishing receptors because there are two Chippewa Bands (the Bad River Band and the Red Cliff Band of Lake Superior Chippewa) who may use Chequamegon Bay as their source of fish. For the HHRA it was conservatively assumed that adult subsistence fishers may be exposed to COPCs via ingestion of locally-caught fish. Although this scenario was selected based on the presence of the two Chippewa Bands, this exposure scenario and the selected exposure parameters are applicable to any subsistence fisher ingesting fish from Chequamegon Bay.

A.3.2 Ecological Receptors and Exposure Scenario

In the BERA (URS, 2006), the potential risk to ecological receptors was evaluated for benthic macroinvertebrates, fish, birds, and mammals. The potential contact points for ecological receptors include surface water, surface soil and food/prey in terrestrial habitats; and, surface water, sediment and food/prey in aquatic and wetland habitats.

Each of these contact points and their respective exposure media were addressed in the BERA.

Routes of Entry

The potential routes of entry for ecological receptors are:

- Direct contact: dermal and/or gill absorption;
- Ingestion; and,
- Inhalation.

In the exposure analysis the relationship between receptors at the Site and potential stressors (chemical, biological, or physical entities that may result in adverse effects to one or more receptors or groups of receptors) were evaluated. Exposure point calculations (EPCs) used to estimate exposure were calculated as the 95% upper confidence limit of the mean (UCL₉₅) of the exposure medium. EPCs calculated for sediment, soil, or tissue residues were based directly upon the levels of contaminants in these media. There were no COPCs for surface water.

Exposure estimates for birds and mammals were calculated using food web models. Simplified food web models were developed to calculate average daily doses (ADDs) of COPCs that representative receptors experience through exposure to sediment, and surface soil at the Site. The ADD represents the dose of a chemical that a receptor may ingest if it foraged within designated exposure units. ADDs for wildlife receptors are calculated using (1) exposure-point concentrations for prey and media developed for each, (2) COPC-specific bioaccumulation

factors or bioaccumulation models for dietary items, and (3) receptor-specific exposure parameters and food chain model assumptions, (e.g., diet composition, foraging area, amount of incidental soil or sediment ingested, etc.).

Risk Characterization

Risk Characterization was the final phase of the BERA. In Risk Characterization, the information from the effects and exposure analyses were used to determine a probability of adverse effects to receptors of concern and discuss the strengths, weaknesses, and assumptions in the BERA. Risk estimates (or Hazard Quotients) were developed for each assessment endpoint based upon comparison of site-specific media concentrations and/or estimated ingested contaminant dose estimates (the latter for wildlife) to effects levels (generic criteria, benchmarks and TRVs) for the various ROCs. Finally risk was characterized for each assessment endpoint by integrating the risk estimate with the results of other lines of evidence, if available.

The results of the risk characterization indicated that there are potentially unacceptable impacts to the benthic macroinvertebrate community in aquatic portions of the Site. Two lines of evidence, bulk sediment chemistry and sediment toxicity testing, indicated that the probability of impairment at the community level was likely. However, the benthic macroinvertebrate community investigation, the one line of evidence that should be accorded the highest weight of evidence, indicated that the benthic macroinvertebrate community at the Site was not impaired relative to benthic communities in reference areas.

The BERA concluded that the potential for adverse effects to ecological receptors other than benthic macroinvertebrates was not sufficient to result in significant adverse alterations to populations and communities of these ecological receptors.

A.3.3 Remedial Action Objectives

The specific goals of the remedial actions are defined by acceptable contaminant levels, or a range of levels at each location for each exposure route. The acceptable contaminant level (or protectiveness) is determined based on the findings of the HHRA and the BERA. The general goal of these objectives is to protect human health and environmental receptors at risk due to constituents at the site. Objectives include:

- Eliminate or reduce to extent practicable potential risk to human health and to aquatic and terrestrial animals and to the environment from exposure to contaminants.
- Eliminate future migration of contaminants to receptors.
- <u>Eliminate</u>, to the extent practicable, on site migration of contaminants.
- Eliminate contamination migration to the Chequamegon bay.
- Remove free product present in the upper bluff (Ravine and NSPW property).
- Remove free product from the lower bluff.

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- Remove free product from the sediments in Chequamegon bay.
- Minimize, to extent practicable, short term risk to human health and to aquatic and terrestrial animals and to the environment from exposure to contaminants during the implementation of the remedial action.

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The HHRA was based upon the protection of human health. The BERA was based upon a risk management goal of maintenance (or provision) of soil, sediment, water quality, food source, and habitat conditions capable of supporting a "functioning ecosystem" for the ecological populations inhabiting or using the Site. The HHRA was used to develop RAOs for soil, and the BERA was used to development RAOs for surface water and sediment. Although HHRA results indicate that groundwater is not used as a potable water supply, construction workers may encounter groundwater in a trench, RAOs for dissolved phase and free-phase (tar) groundwater contamination were also developed for groundwater. The development of RAOs is described in the following sections. RAOs for site media are summarized below.

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Remedial Action Objective Summary by Site Media

Environmental Media	Receptor	SERemedial Action Objectives		
		Protect human health by eliminating exposure		
		(direct contact, ingestion, inhalation) to	1 ~	
		groundwater with COPCs in excess of		Peleted: event ingestion of water aving
	Human Health	regulatory or risk-based standards.		Deleted: MCLs and/or that pose a
	1	Reduce contaminant levels in groundwater to	Пех	ealth risk
	1	meet MCLs and State of Wisconsin Drinking	1	
Groundwater		Water Standards.	_	
		Protect the environment by controlling the off-	1	
	ļ	site migration of contaminants in the	1	
	Environment (Ecological	groundwater to surrounding surface water		
	Receptors)	bodies which would result in exceedance of	1	
		ARARs for COCs in surrounding surface	1 _	
		waters.	1	
	1	Conduct free product removal whenever it is		
		necessary to halt or contain the discharge of a	1	
		hazardous substance or to minimize the harmful	1	
		effects of the discharge to the air, land or water.	1	
Soil	Human Health	Protect human health by reducing or	1 ~	
	Human ricalin	eliminating exposure (ingestion/direct	1 D	Peleted: event

		contact/inhalation) to soil having COPCs		Deleted: of
		representing an excess cancer risk greater than		
		10-6 as a point of departure (with cumulative		
,		excess cancer risks not exceeding 10 ⁻⁵) and a		
		hazard index (HI) greater than 1 for reasonably		
		anticipated future land use scenarios.		Deleted: which pose an unacceptable
		Ensure future beneficial commercial/industrial	<i>→</i> '	health risk.
		use of the site and recreational use of Kreher		
		Park.		
		Protect populations of ecological receptors or		
		individuals of protected species by eliminating		
		exposure (direct contact with or incidental		Deleted: event
		ingestion of soils or prey) to soil with levels of		Deleted: having
		COPCs that would pose an unacceptable risk,		Deleted: to
		Conduct free product removal whenever it is		Deleted: populations of ecological receptors or individuals of protected
	Environment (Ecological	necessary to halt or contain the discharge of a		species.
	Receptors)	hazardous substance or to minimize the harmful		
		effects of the discharge to the air, land or water.		
		Protect the environment by		
		minimizing/eliminating the migration of		
		contaminants in the soil to groundwater or to		
		surrounding surface water bodies.		
		Protect human health by minimizing exposure		
		(direct contact, ingestion, inhalation) to surface		
		water that has been impacted by Site-related		
	Human Health	groundwater and sediment with concentrations		
		of COPCs such that regulatory or risk-based		
		surface water standards have been exceeded.		Deleted: event ingestion of water having COPCs in excess of MCLs and/or
Surface Water		Protect the environment by controlling the		that pose a health risk
		migration of contaminants in groundwater and		
	Environment (Ecological	in sediments to surface water which would		
	Receptors)	result in exceedance of ARARs for COPCs in		
	*	surface water.		Deleted: Ecological Receptors
		Reduce site-related COPC levels in the surface		
		water to meet the State of Wisconsin Surface		

		Water Quality Standards,
	Human Health	Protect human health by eliminating exposure (direct contact, ingestion, inhalation, fish ingestion) to sediment with COPCs in excess of regulatory or risk-based standards
Sediments	Environment (Ecological Receptors)	Conduct free product removal whenever it is necessary to halt or contain the discharge of a hazardous substance or to minimize the harmful effects of the discharge to the air, land or water. Protect populations of ecological receptors or individuals of protected species by eliminating exposure (direct contact with or incidental ingestion of sediment or prey) to sediment with levels of COPCs that would pose an unacceptable risk.

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This includes industrial, commercial, and utility worker protection and protection of recreational users of Kreher Park. The basis and rationale for groundwater remediation objectives is based on anticipated commercial/industrial and recreational land use. These objectives were developed to eliminate exposure and protect against off-site migration of contaminants. The basis and rationale for surface water remedial objectives are to minimize the potential for contaminant exposure to surface water users and reduce migration of groundwater and sediment contaminants to surface water that could result in excedance of surface water standards. The basis and rationale for sediment remedial objectives are to protect the fishery and populations of aquatic organisms and to protect against migration of contaminants into surface water.

A.3.3.1 HHRA Based Remedial Action Objectives for Soil, Surface Water and Groundwater

The results of the HHRA indicate that only residential exposure pathways (for soil depths between 0 to 3 feet or all soil depths to 10 feet bgs) and construction worker exposure pathways (for soil depths between 0 and 10 feet) are associated with unacceptable risks (Cancer Risk (CR) greater than 10⁻⁴ and Hazard Index (HI) greater than 1) based on exposures to soil in the filled ravine area for residential receptors and the Kreher Park area for construction worker receptors. However, residential receptors are not expected to be exposed to subsurface soil given the current and potential future land use of the Site. (Residential land use in Kreher Park is not anticipated, and residential land use in the upper bluff area is located outside the backfilled ravine where contamination has been identified.) For this Site, risks associated with exposures to

surface soil are within acceptable risk ranges.

Although the results of the HHRA indicate risks for exposure to soils and the construction worker scenario exceed USEPA acceptable levels, the assumptions used to estimate risks to this receptor were conservative and considered the worst case. Risk for exposure to groundwater by construction workers was not calculated, but is likely to exceed PRGs. Given both the current and future land use of the Site, it is not likely that construction workers would be exposed to subsurface soil at depths beyond 4 feet bgs (a typical depth for the installation of underground utility corridors), as most activities associated with the implementation of the future land use would be associated with subsurface activities such as regrading, landscaping, and road or parking lot construction. Therefore, risks to this receptor population are most likely overstated.

Risks to recreational users (surface soil), waders and swimmers (sediments), industrial workers (surface soil), and maintenance workers (surface soil) are all within USEPA's acceptable range of 10^{-4} to 10^{-6} (and do not exceed a cumulative risk of 10^{-5}) for CR and 1 for HI. Risks to subsistence fishers (finfish) was at 10^{-4} and risk to a wader contacting surface water ranged from 2×10^{-5} to 6×10^{-5} .

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Preliminary Remediation Goals for Soils and Surface Water

Based on the results of the Site-specific HHRA, preliminary remediation goals (PRG) were derived for the following exposure scenarios that exceeded a cumulative cancer risk of 10⁻⁵ a cumulative noncancer risk of a hazard index (HI) of 1:

- Construction worker exposure to soil at Krehler Park
- Residential exposure to soil at the Upper Bluff
- Recreational exposure to surface water

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PRGs were derived for chemicals identified as the primary risk drivers using exposure parameters that were used to develop the HHRA. Presented below are chemical-specific acceptable contaminant levels for these exposure scenarios based on target cancer risk goals of 10^{-4} to 10^{-6} and target noncancer risk goals of an HI of 0.1 and 1. PRGs are not developed for fish because remediation is not plausible for fish; rather, risks from fish consumption is controlled through consumption advisories and fish contaminant levels will be reduced through sediment remediation. PRGs were not developed for the indoor air pathway; rather, indoor air levels will be reduced through groundwater remediation.

Soil Preliminary Remediation Goals for Construction Workers (mg/kg)						
	Carcinogenic	Noncarcinogenic Noncarcinogeni				
<u>Chemical</u>	Effects	Effects				

Comment [D2]: There is NO supporting documentation in the KAQ or HIRA that describes how these PRGs were derived. Either the specific reference or calculations are needed before the below PRGs can be accepted. I assume these were obtained or derived from the EPA Region 9 PRG Tables and edits were made taking this into account.

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	$ _{CR=10^{-}} $	$CR = 10^{-}$	$CR = 10^{-1}$			
	6	<u>5</u>	4	$\mathbf{HI} = 0.1$	<u>HI = 1</u>	
SVOCs						
2-Methylnaphthalene	<u>N</u> A	<u>NA</u>	<u>NA</u>	1.13E+02	1.13E+03	
Benzo(a)anthracene	2.01E+00	2.01E+01	2.01E+02	1.06E+04	1.06E+05	
Benzo(a)pyrene	2.01E-01	2.01E+00	2.01E+01	<u>NA</u>	<u>NA</u>	
Benzo(b)fluoranthene	2.01E+00	2.01E+01	2.01E+02	<u>NA</u>	<u>NA</u>	
Dibenzo(a,h)anthracene	2.01E-01	2.01E+00	2.01E+01	<u>NA</u>	<u>NA</u>	
Indeno(1,2,3-cd)pyrene	2.01E+00	2.01E+01	2.01E+02	7.06E+03	7.06E+04	
<u>Naphthalene</u>	<u>NA</u>	<u>NA</u>	<u>NA</u>	3.81E+00	3.81E+01	
VOCs						
Benzene	1.4E+00	1.4E+01	1.4E+02	4.11E+00	4.11E+01	

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Charata at	Carcinog	enic Effects	Noncarcinogenic Effects		
Chemical	$CR = 10^{-5}$ $CR = 10^{-4}$		HI = 0.1	HI = 1	
SVOCs					
Benzo(a)anthracene	6.21E+00	6.21E+01	NA	NA_	
Benzo(a)pyrene	6.21E-01	6.21E+00	NA	NA_	
Benzo(b)fluoranthene	6.21E+00	6.21E+01	NA	NA_	
Dibenzo(a,h)anthracene	6.21E-01	6.21E+00	NA	NA	
Naphthalene	NA	NA	1.70E+00	1.70E+01	
VOCs					
Benzene	7.37E+00	7.37E+01	1.80E+00	1.80E+01	

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Comment [D9]: Source of PRG not identified

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Carcinogenie Effects	Formatted: Strikethrough Formatted: Strikethro
Chemical 10 10 10 10 10 11 11 1	Formatted: Strikethrough Formatted: Strikethro
Chemical 10 10 10 10 10 11 11 1	Formatted: Strikethrough Formatted: Strikethro
Chemical 10 ⁻⁶ 10 ⁻⁶ 10 ⁻⁴ HI = 0.1 HI = 1	Formatted: Strikethrough Formatted: Strikethro
Mathylaphthalene	Formatted: Strikethroug
Mathylanephthalene	Formatted: Strikethroug
1.06E+01 1.06E+02 1.06E+03 1.06E+04 1.06E+05 1.020(a)pyrene 2.42E+00 2.42E+01 2.42E+02 NA	Formatted: Strikethroug
2.42E+00 2.42E+01 2.42E+02 NA	Formatted: Strikethroug Formatted: Strikethroug Formatted: Strikethroug Formatted: Strikethroug Formatted: Strikethroug Formatted
2.42E+01 2.42E+02 2.42E+03 NA	Formatted: Strikethroug Formatted: Strikethroug Formatted: Strikethroug Formatted: Strikethroug
Penze(a,b)anthracene 2.42E+00 2.42E+01 2.42E+02 2.42E+03 7.06E+03 7.06E+04 Solid Preliminary Remediation Goals for Residents (mg/kg)	Formatted: Strikethroug Formatted: Strikethroug Formatted: Strikethroug
Preliminary Remediation Goals for Residents (mg/kg) Noncarcinogenic	Formatted: Strikethroug Formatted
NA NA NA 3.81E+01 4.11E+01 4.11E+01 4.11E+01 3.81E+01 3.81E+01 4.11E+01 4.11E	Formatted: Strikethroug
Soil Preliminary Remediation Goals for Residents (mg/kg)	Formatted
Soil Preliminary Remediation Goals for Residents (mg/kg)	
Soil Preliminary Remediation Goals for Residents (mg/kg)	f
Noncarcinogenic Carcinogenic Effects Effects	Formatted: Strikethrough
Carcinogenic Effects Effects	Formatted: Strikethrough
Carcinogenic Effects Effects	Formatted: Strikethrough
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Carcinogenic Effects Effects	Formatted: Strikethrough
Carcinogenic Effects Effects CR = CR = CR = 10-6 CR = 10-6 CR = 10-6 HI = 0.1 HI = 1 Cs e(a)anthracene 6.21E 01 6.21E+00 6.21E+01 NA NA NA NA e(a)pyrene 6.21E 02 6.21E 01 6.21E+00 NA NA NA NA e(b)fluoranthene 6.21E 01 6.21E+00 6.21E+01 NA NA NA NA hazo(a,h)anthracene 6.21E 02 6.21E 01 6.21E+00 NA NA NA NA thalene NA NA NA NA 1.70E+00 1.70E+01	Formatted: Strikethrough
CR = 10 ⁻⁶ CR = 10 ⁻⁵ CR = 10 ⁻⁴ HI = 0.1 HI = 1 Cs O(a)anthracene 6.21E 01 6.21E +00 6.21E +01 NA NA O(a)pyrene 6.21E 02 6.21E 01 6.21E +00 NA NA O(b)fluoranthene 6.21E 01 6.21E +00 6.21E +01 NA NA nzo(a,h)anthracene 6.21E 02 6.21E 01 6.21E +00 NA NA thalene NA NA NA 1.70E +00 1.70E +01	
Chemical 10-6 10-5 10-4 HI = 0.1 HI = 1 Cs 0(a)anthracene 6.21E 01 6.21E +00 6.21E +01 NA NA 0(a)pyrene 6.21E 02 6.21E 01 6.21E +00 NA NA 0(b)fluoranthene 6.21E 01 6.21E +00 6.21E +01 NA NA nzo(a,h)anthracene 6.21E 02 6.21E 01 6.21E +00 NA NA thalene NA NA NA 1.70E +00 1.70E +01	
Cs e(a)anthracene 6.21E 01 6.21E+00 6.21E+01 NA NA e(a)pyrene 6.21E 02 6.21E 01 6.21E+00 NA NA e(b)fluoranthene 6.21E 01 6.21E+00 6.21E+01 NA NA ezo(a,h)anthracene 6.21E 02 6.21E-01 6.21E+00 NA NA thalene NA NA NA 1.70E+00 1.70E+01	
o(a)anthracene 6.21E 01 6.21E+00 6.21E+01 NA NA o(a)pyrene 6.21E 02 6.21E 01 6.21E+00 NA NA o(b)fluoranthene 6.21E 01 6.21E+00 6.21E+01 NA NA nzo(a,h)anthracene 6.21E 02 6.21E 01 6.21E+00 NA NA thalene NA NA NA 1.70E+00 1.70E+01	Formatted: Strikethrough
e(a)pyrene 6.21E-02 6.21E-01 6.21E+00 NA NA e(b)fluoranthene 6.21E-01 6.21E+00 6.21E+01 NA NA nzo(a,h)anthracene 6.21E-02 6.21E-01 6.21E+00 NA NA thalene NA NA NA 1.70E+00 1.70E+01	Formatted: Strikethrough
o(b)fluoranthene 6.21E-01 6.21E+00 6.21E+01 NA NA nzo(a,h)anthracene 6.21E-02 6.21E-01 6.21E+00 NA NA thalene NA NA NA 1.70E+00 1.70E+01	Formatted: Strikethrough
o(b)fluoranthene 6.21E-01 6.21E+00 6.21E+01 NA NA nzo(a,h)anthracene 6.21E-02 6.21E-01 6.21E+00 NA NA thalene NA NA NA 1.70E+00 1.70E+01	Formatted: Strikethrough
hzo(a,h)anthracene 6.21E 02 6.21E 01 6.21E+00 NA NA thalene NA NA NA 1.70E+00 1.70E+01	Formatted: Strikethrough
thalene NA NA 1.70E+00 1.70E+01	Formatted: Strikethrough
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ene 7.37E 01 7.37E+00 7.37E+01 1.80E+00 1.80E+01	Formatted: Strikethrough

Surface Water Preliminary Remediation Goals for Swimmers (mg/L)							
	Noncarcinoger Carcinogenic Effects Effects						
<u>Chemical</u>	$CR = 10^{-6}$	$\underline{\mathbf{CR}} = 10^{-5}$	$CR = 10^{-4}$	HI = 0.1	<u>HI = 1</u>		
<u>SVOCs</u>							
Benzo(a)anthracene	2.04E-04	2.04E-03	2.04E-02	<u>NA</u>	<u>NA</u>		
Benzo(a)pyrene	1.17E-05	1.17E-04	1.17E-03	<u>NA</u>	<u>NA</u>		
Benzo(b)fluoranthene	1.19E-04	1.19E-03	1.19E-02	<u>NA</u>	<u>NA</u>		
Dibenzo(a,h)anthracene	7.72E-06	7.72E-05	7.72E-04	<u>NA</u>	<u>NA</u>		
Indeno(1,2,3-cd)pyrene	1.17E-04	1.17E-03	1.17E-02	<u>NA</u>	<u>NA</u>		

Preliminary Remediation Goals for Groundwater

No COPCs were <u>initially</u> identified in the HHRA for groundwater because <u>groundwater is not</u> used as a <u>potable water supply</u>. However, exposure to contaminated groundwater and accompanying NAPLs can potentially occur via the following exposure scenarios:

- Construction worker exposure to shallow groundwater infiltrating trenches at Kreher Park
- Trespasser exposure to groundwater infiltrating the lower level of the former Waste
 Water Treatment Plant in Kreher Park

These pathways are further discussed and the PRGs for direct contact and inhalation of vapors from affected groundwater are presented under section A.3.3.3 (Remedial Action Objectives for Media with No Exposure Pathways).

The COPCs in sediment included five PAHs, but the cumulative risks estimated for the recreational receptor exposures to sediments were below USEPA's target risk levels.

A.3.3.2 BERA Based Remedial Action Objectives for Sediment

The BERA effects analysis consisted of an evaluation of available toxicity or other effects information used to relate the exposure estimates to a level of adverse effects. Risk Characterization was the final phase of the BERA. The effects and exposure analyses were used to determine a probability of adverse effects to receptors. Risk estimates (or Hazard Quotients) were developed for each assessment endpoint based upon comparison of site-specific media concentrations and/or estimated ingested contaminant dose estimates to effects levels (generic criteria, benchmarks and toxicological reference values for the various receptors. Finally risk was characterized for each assessment endpoint by integrating the risk estimate with the results of

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pathways.

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other lines of evidence, if available.

Toxicity tests performed as part of the BERA indicated the potential for impairment to the benthic macroinvertebrate community in aquatic portions of the Site, as evidenced by pronounced toxicity in laboratory toxicity tests. Effects observed from field surveys of the existing benthic community indicated effects that were less dramatic than those demonstrated in the laboratory toxicity studies, but interpretation of the field survey data is made very difficult by a high degree of variability and lack of comparability between reference and site stations.

In addition, the sporadic release of free phase hydrocarbons from Site sediment during high energy meteorological events or when disturbed by other activities may result in episodic conditions that may limit the functionality of the aquatic community in the Site area. If normal lake front activities, i.e., wading, boating etc., were not presently prohibited, the disturbance of sediments and release of subsurface contaminants would increase. This potentially could lead to greater impacts than were measured during these RI/FS studies.

The BERA concluded that the potential for adverse effects to ecological receptors other than the benthic community was limited. Therefore the only PRG proposed is for the benthic community exposed to COPCs in sediment. Since PAHs are the most widespread COPCs at the Site and are the basis for most of the potential risk to ecological receptors these have been the focus of the BERA. A PRG focused on PAHs in sediment will address potential risk from other Site COPCs in sediment.

There were no COPCs in Site soil or surface water that contributed to unacceptable <u>ecological</u> risk.

Preliminary Remediation Goals

It was determined that levels of PAHs in sediments were the most significant contributor of potential risk to ecological receptors at the Site. Based upon the results of the BERA, exposure of ecological receptors to COPCs in groundwater and soils is not expected to result in unacceptable effects to populations of valued ecological receptors. There were only occasional low level detections of benzene, ethylbenzene, toluene and naphthalene in the filtered fraction of Site surface water and none of these detections exceeded screening criteria. No other COPCs were detected.

The overall goal for sediments at the Ashland site is protection of the survival, growth, and reproduction of benthic invertebrate communities. The thresholds presented herein were derived from data collected through all iterations of sediment investigation at the site and is based on a best professional evaluation of sediment chemistry, bioassay, and benthic community study data collected by SEH and NSPW as well as draws upon the considerable body of information on PAH toxicity to benthic organisms to supplement the site data. Due to the uncertainty associated

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with the benthic community studies, it was concluded to not include this information in the discussion of PRGs. The range of threshold values discussed below was found to be consistent with the distribution of site data and external chemical benchmarks.

Calculation of Thresholds for Benthic Species Tested for Ashland BERA

From the available data, it appears that of the three benthic species used in sediment toxicity tests, the midge *Chironomus dilutus* (formerly *tentans*) is the most sensitive. This is supported by both the comparative toxicity in sediment dilution series tested by SEH (2001) and by the literature data for water-only toxicity of fluoranthene reported by Schuler et al (2004; ES&T 38:6247). Therefore, if the goal is to derive an RAO that will protect these three species, then it is the toxicity threshold for midge that will set the threshold.

The first issue is to define what the threshold will be. Statistical significance is sometimes used-to define toxicity thresholds, but this can be problematic because it is defined in large part by the concentrations tested and subtleties in data variability, neither of which is relevant to the expected biological effect of exposure. In recent years, greater emphasis has been placed on estimating specific levels of effect using various regression techniques. For this purpose, a 20 percent effect threshold (EC20) is often chosen. While it is difficult to establish whether this is a true "threshold" for adverse effect (i.e., all concentrations below this are "safe"), it becomes difficult to reliably estimate levels of effect lower than this. It also corresponds to a level of effect that is commonly found to be significant in toxicological testing. In selecting the EC20, it is recognized that this does not guarantee the absence of biological effect at this concentration; however, it will be presumed that levels of effect lower than this will be adequately addressed through natural attenuation of residual effects.

Within the toxicity tests conducted for the Ashland BERA, there is only one test that directly-determines an EC20 for midge; that was the sandy sediment dilution test by SEH (2001). While this is in some ways the most direct method for estimating this value, this study has been criticized repeatedly by Xcel/URS because of anomalies in the analytical data that make the reported exposure concentrations somewhat uncertain. As a cross check on this value, one can use the larger body of available data to make estimates of the midge EC20 using responses in other tests and relationships among endpoints. The details of this analysis are described in detail in Attachment A, and are summarized in the table below. Estimates of the midge EC20 range from 1340 to 3930 ug PAH/g OC; converting to a dwt basis assuming a sediment OC of 0.415%, this corresponds 5.57 to 16.3 ug PAH/g dwt. Because of the uncertainties involved, it may be most appropriate to think of the midge EC20 as a range rather than a single value.

Summary of Midge EC20 Estimates

<u>Concentration</u>	ug PAH/g dwt.	Summary of Derivation
(ug PAH/g OC)	@ 0.415% OC	_

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		Treat SQT7 as Hyalella 28-d LC80; adjust from
		Hyalella 28-d LC80 to midge LC20 based on SEH
<u>1340</u>	<u>5.57</u>	(2001) dilution studies.
		Treat SQT7 as Hyalella 28-d LC80; adjust from
		Hyalella 28-d LC50 based on URS (2006) and SEH
		(2001) dilution studies; adjust to midge LC50 based
ļ		on Schuler (2004); adjust from midge LC50 to
<u>1770</u>	<u>7.35</u>	midge LC20 based on SEH (2001) dilution studies.
		Midge LC50 predicted from Schuler (2004);
1)		adjustment from LC50 to LC20 based on SEH
2020	8.38	(2001) dilution study.
		Hyalella 10-d LC50 from URS (2006) dilution
		study; adjust from Hyalella 10-d LC50 to midge
		LC50 based on Schuler (2004); adjust midge LC50
		to midge LC20 based on SHE (2001) dilution
<u>2560</u>	<u> 10.6</u>	studies.
		Average of LC20 and EC20 from SEH (2001) test
<u>3930</u>	<u>16.3</u>	with dilutions of contaminated sandy sediment.

Note that these values are still not as low as the calculated EPA ESB concentration of 557 ug-PAH/g OC (2.31 ug PAH/g dwt at 0.415% OC). Among the reasons for this is that the EC20 midge is the lowest value from among three species, and would not necessarily protect even more sensitive species. Basing an RAO on the midge EC20 should be done in recognition that effects to highly sensitive organisms are possible, and may require additional attenuation of exposure over time to meet a more stringent definition of "threshold."

Based on the various data sources, the EC20 for midge is expected to lie within a range of 1340-to 3930 ug PAH/g OC. At an organic carbon (OC) of 0.415%, this corresponds to a range of 5.6 to 16.3 ug PAH/g dwt. The proposed PRG for sediment is 2,295 ug PAH/g OC (9.5 ug PAH/g dwt at 0.415% OC), which is the geometric mean of the above range. For purposes of converting to a dry weight concentration so it can be applied equally throughout the Site, an organic carbon concentration of 0.415% was assumed for all Site sediment. Sampling by URS both on and off site clearly indicates OC contents well below 1% in sandy sediments. The mean of the OC measured in SQT1 and SQT7 is 0.415%. Whether this is the exact value that should be used probably warrants further evaluation, though it is clear that something lower than 1% is necessary to accurately reflect the toxicity of sandy site sediments.

This PRG does not include the added effects of UV and is based on a water depth of 6 feet or

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Levels¶

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Formatted: Font: (Default) Times New Roman, 12 pt, Not Bold, Not Highlight more. If the final depth of sediments will be less than 6 feet, the PRG for any active remedial intervention will be adjusted downward as based upon UV extinction coefficients measured in Site waters. The adjusted PRGs (assuming no debris cover) are provided in the following table:

Water Depth	% of Surface Irradiance at Depth	24-h Average Irradiance	PAH at LC20 (ug/g OC)	PAH at LC20 (ug/g dwt @ 0.415% OC))
(cm)		(µW/cm2)		No Debris
	88.1	<u>860.6</u>	143	0.59
<u>,10</u>	<u>81.8</u>	<u>799.5</u>	<u>154</u>	<u>0.64</u>
<u>25</u>	<u>65.6</u>	<u>640.9</u>	<u>192</u>	0.8
<u>50</u>	<u>45.4</u>	<u>443.4</u>	277	<u>1.15</u>
<u>,100</u>	21.7	212.2	<u>579</u>	<u>2.4</u>
<u>,150</u>	10.4	<u>101.6</u>	<u>1210</u>	<u>5.02</u>
200	<u>4.98</u>	<u>48.6</u>	2530	<u>10.5</u>
<u>232</u>	<u>3.11</u>	<u>30,3</u>	<u>4050</u>	<u>16.8</u>
<u>250</u>	2.38	<u>23.3</u>	5280	<u>21.9</u>
<u>300</u>	1.14	<u>11.1</u>	11000	<u>45.8</u>

This PRG would prevent direct contact with or ingestion of sediments or prey having levels of COPCs that would pose an unacceptable risk to populations of ecological receptors or individuals of protected species. The following factors support that conclusion:

- 1) This PRG meets the RAO because it protects populations of wildlife and fish.
 - a. The results of the BERA indicated that even under baseline conditions populations of wildlife, including waterfowl, would not be exposed to unacceptable risk of harm. Therefore, wildlife would be protected at a PRG of 2.295 ug PAH/g OC (9.5 ug PAH/g dwt at 0.415% OC)] since this is substantially less than the baseline conditions to which they are presently exposed.
 - b. The results of the BERA indicated that even under baseline conditions, adult fish were not directly exposed to sufficient levels of PAHs nor did they accumulate sufficient PAHs to pose a risk of harm. The sediment bioassay using the fathead

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minnow indicated the threshold for effects is greater than 60.8 µg tPAH/g @1%OC and perhaps as high as 363.0 µg tPAH/g @1%OC. The SEH dilution bioassay indicated an EC20 of around 94.0 µg tPAH/g @1%OC (based upon USEPA's analysis). Based upon these two lines of evidence fish populations should not be exposed to risk of harm if a PRG of 2.295 ug PAH/g OC (9.5 ug PAH/g dwt at 0.415% OC)] were used since this is substantially less than the baseline conditions to which they are presently exposed.

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2) This PRG protects benthos at the population and community level. USEPA has provided squidance that except for protection of the individuals of species of special concern, such as threatened and endangered species, protection of populations and communities of biota is the basis for a clean-up standard based upon risk to ecological receptors.

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a. Use of the EC20 is consistent with the data quality objective (DQO) for sediment bioassays which states: "If control survival is = 80%, and the difference between Site survival or growth and reference station survival or growth is = 20% (statistically significant difference at a = 0.1) it is indicative of unacceptable risks" (25 January 2005 BERA, Appendix G, Table 4. Data Quality Objectives for 28 day Hyalella azteca (Amphipod) with and without UV Light and 20-day Chironomus dilutus (formerly C. tentans) (Midge) Sediment Bioassay).

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b. The range of estimated midge EC20 values is consistent with the distribution of site data and external chemical benchmarks. Figure 1 shows a summary of all available toxicity data for solid-phase toxicity testing of sandy sediments from the Ashland site (in the absence of UV light), combining data from SEH (1998), SEH (2001), and URS (2006). Also shown are WDNR TEC, MEC, and PEC effect endpoints, the EPA ESB value, and the range of midge EC20 estimates listed in the above Table. As can be seen, the midge EC20 range lies in an area that is consistent with the distribution of toxic and nontoxic samples; that is, most of the toxic samples lie to the right of this range, and most of the non-toxic samples lie to the left. Also obvious is the very limited amount of toxicological data in the critical range of PAH concentrations, primarily 600 to 6000 ug/g organic carbon. Finally, the midge EC20 range is consistent with midrange of the WDNR guidance values.

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However, as we have concluded from USEPA's comments that protection of even individual organism in a small portion of the benthic community is of importance, NSPW

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Summary:

A two-tiered sediment PRG is proposed to meet the RAOs in Table 1.

¹ USEPA Ecological Risk Assessment and Risk Management Principles for Superfund Sites (OSWER Directive 9285.7-28 P) indicates that, "Superfund remedial actions generally should not be designed to protect organisms on an individual basis (the exception being designated protected status resources, such as listed or candidate threatened and endangered species or treaty-protected species that could be exposed to site releases), but to protect local populations and communities of biota." (USEPA 1999).

- 1) Sediments in greater than 6 feet of water having a concentration greater than 2.295 ug PAH/g OC (9.5 ug PAH/g dwt at 0.415% OC) and sediments in 6 feet or less of water having a concentration greater than a UV-adjusted PRG will be addressed with an active remedial intervention, i.e., by either removing or covering them to terminate any exposure pathways; and
- 2) Sediments in greater than 6 feet of water having a concentration equal or less than 2,295 ug PAH/g OC (9.5 ug PAH/g dwt at 0.415% OC) and sediments in 6 feet or less of water having a concentration greater than a UV-adjusted PRG, will be monitored to assure that there are no unacceptable impacts to benthic community and that the levels of PAHs in surface sediments decrease over time to 1340 ug PAH/g OC (5.6 ug PAH/g dwt at 0.415% OC), which is the lower of the range of midge EC20 values based on site data.

In addition, although these conditions will likely address all sediments where there is free phase, the PRG is amended to explicitly provide for the removal of all sediments associated with free phase even if they occur in areas where PAH concentrations are lower than the proposed PRG of 2,295 ug PAH/g OC (9.5 µg tPAH/g @ 0.415%OC).

This proposed PRG is supported by and further defined by the following information:

- This two-tiered PRG will be applied to all sediments (both sediments that are primarily wood as well as those that are primarily sand).
- This PRG is based upon total PAHs as defined in the BERA. These are the sum of 24 PAHs used by NOAA in its Status and Trends program. Because effects levels for bioassays as well for the benthic community analysis were based upon the same 24 PAHs as were measured in the bulk sediment analysis, the 24 PAHs can represent all PAHs, measured and unmeasured. Only the assumption that the relative proportion of non-Status and Trends PAHs to all PAHs remains relative constant need be made. All non-detect PAHs will be included in the total calculation at one-half the detection limit, which is consistent with the approach used in the BERA.
- __The proposed PRG will be applied to all sediments regardless of the <u>sediment</u> depth. Obviously this only makes a difference for removal alternatives.
- The sediment bioassays indicated that UV light caused increased toxicity to laboratory organisms. For sediments in depths of less than six feet, the PRG for any active remedial intervention will be adjusted downward as directed by USEPA based upon UV extinction coefficients measured in Site waters. Adjusted PRGs are shown above.

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For purposes of converting the 53 μg tPAH/g @1%OC or the 12.2 μg tPAH/g @1%OC to a dry weight concentration so tt can be applied equally throughout the Site, an organic carbon concentration of 1% will be assumed for all Site sediment. Figures A-1 and A-2 show that most Site sediment has an organic carbon content of at least 1%. Therefore, the two

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In summary, a two-tiered sediment cleanup level is recommended. A sediment cleanup level of 9.5 µg tPAH/g dwt will be used as the basis for implementing active remedial intervention. In addition sediments exceeding 5.6 µg PAH/g dwt, which is the lower of the range of midge EC20 values based on site data, but less than or equal to the cleanup level of 9.5 µg tPAH/g dwt will be monitored to assure that there are no unacceptable impacts to benthic community and that the levels of PAHs in the surface sediments to which the benthic is exposed decreases over time to at least this lower EC20 threshold. The Remedial Action Plan will include specific performance objectives for monitoring the Site sediments in the concentration range of from 5.6 µg PAH/g to 9.5 µg tPAH/g. The Remedial Action Plan will also include contingencies that will be implemented if the performance objectives for Natural Recovery of these sediments to levels lower than the lower EC20 threshold does not occur.

These proposed PRGs assure that all sediment RAOs in Table 1 including protection of humans, wildlife, fish and the benthic community are met.

A.3.3.3 Remedial Action Objectives for Media with No Exposure Pathways

As described in Section A.3.1.3 above, currently groundwater is not used as a potable water supply, in the vicinity of the Site. Potential exposure to shallow groundwater encountered in Kreher Park fill was eliminated when the seep area was capped in 2002. Shallow groundwater encountered in the filled ravine and groundwater in the underlying Copper Falls aquifer are not currently being used for drinking water in the vicinity of the Site². However, construction workers in a trench may be exposed to groundwater contaminants. For any trench excavated at Kreher Park, shallow contaminated groundwater and NAPLs can easily infiltrate through coarse fill materials and workers who enter the trenches can be exposed through direct dermal contact and inhalation of vapors. At the former WWTP, trespassers who enter buildings can potentially inhale vapors and have direct dermal contact with contaminated groundwater and NAPLs that have infiltrated the flooded lower level of the facility. The potential health risks associated with these exposure pathways have not been thoroughly evaluated by the HHRA and is a data gap, but direct contact exposures to NAPL or "free-product" in groundwater may pose an unacceptable health risk.

Despite these data gaps, site investigation results indicate that COPCs in the shallow Kreher Park and ravine fill units, and groundwater in the underlying Copper Falls aquifer exceed regulatory enforceable groundwater quality standards. PRGs for groundwater were derived primarily from Wisconsin Administrative Code (WAC) chapter NR 140 groundwater quality standards for the most frequently occurring dissolved phase organic COPCs based on historic groundwater monitoring results. The concentrations provided in the table below provide a conservative level

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Although no contaminants were detected in samples collected from two artesian wells located in Kreher Park that obtain water from the Copper Falls aquifer, the City of Ashland restricted access to these wells for public use in August 2004. Additionally, the Site is located within the City limits and serviced by a municipal water supply.

that will be further refined in subsequent technical memoranda and the FS.

<u>Preliminary Remediation Goals</u> (µg/l) for Organic COPCs in Groundwater (WAC Chapter NR 140 Enforcement Standard)

E GORC YOUR	ES.	COPC-SYOCE	E CES
Benzene	5	Anthracene (LMW)	3,000
Ethylbenzene	700	Benzo(a)Pyrene (HMW)	0.2
Styrene	100	Benzo(b)Fluoranthene (HMW)	0.2
Toluene	1,000	Chrysene (HMW)	0.2
1,2,4-Trimethylbenzene	480 ²	Fluoranthene (HMW)	400
1,3,5-Trimethylbenzene	460	Fluorene (LMW)	400
Total Xylenes	10,000	Naphthalene (LMW)	40
		Pentachlorophenol	1
		Pyrene (HMW)	250
		Phenol	6,000

^{1 (}HMW) - Heavy molecular weight PAHs; (LMW) - Low molecular weight PAHs

Inorganic COPCs (metals and cyanide) were also detected above groundwater quality standards. Acceptable contaminant levels for groundwater were derived primarily from WAC chapter NR 140 groundwater quality standards for the most frequently occurring dissolved phase inorganic COPCs based on historic groundwater monitoring results. However, iron and manganese were detected in samples collected from up gradient wells³ at concentrations above groundwater quality standards. Because these elevated concentrations represent background conditions, the maximum detected concentrations have been substituted as the acceptable contaminant level for COPCs that exceed groundwater quality standards in background samples. A summary of the acceptable contaminant levels for inorganic COPCs in the Miller Creek and Copper Falls aquifer follows: The concentrations provided in the table below provide a conservative level that will be further refined in subsequent technical memoranda and the FS.

Trimethylbenzene (TMB) in groundwater will be presented as the sum of 1,2,4- and 1,3,5- TMB per the WAC ch. NR 140 standard.

³ Samples collected from well MW-11 located outside the ravine fill represents background conditions for shallow groundwater in the upper bluff area, and samples collected from MW-6A represent background conditions for the underlying Copper Falls aquifer.

Preliminary Remediation Goals (μg/l) for Inorganic COPCs in Groundwater

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Inorganics ES		Background Concentrations for Miller Creek (Well MW-11)	Background Concentrations for Copper Falls (Well MW-6A)				
Arsenic	6	0-3.2	0 – 4.4				
Antimony	10	0-4.3	0 – 4.1				
Barium	2,000	130 – 260	640 – 710				
Beryllium	4	ND	ND				
Cadmium	5	0-0.2	ND				
Chromium (+3)	1001	ND	0.87 – 2.1				
Chromium (+6)	100	ND	0.07 - 2.1				
Cobalt	40	0 – 16	0-1.1				
Copper	1,300	2-35	2.4 – 6.1				
Cyanide	200	0-17	0-4				
Iron	300	7.1 – 19,000	0 – 0.0046				
Lead	15	0-3.3	0.485 – 2.6				
Manganese	50	13 – 760	30 – 410				
Mercury	2	ND	ND				
Nickel	100	0.95 – 24	1.6 – 4.7				
Selenium	50	0-3.3	0-2.8				
Silver	50	0 – 1.65	0-0.8				
Thallium	2	ND	ND				
Vanadium	30	2.1 – 38	9 – 10				
Zinc	5,000	0 - 59	0 – 17				

Chromium in groundwater will be presented as total chromium per the WI ch. NR 140 standard

Free phase hydrocarbons (tar) encountered in the Kreher Park fill, ravine fill, NSPW property and Copper Falls aquifer are behaving as a source for the dissolved phase plumes identified in each unit at the Site. PRGs for free-phase tar are within these units are based on WAC NR 708.13, which states the following:

Responsible parties shall conduct free product removal whenever it is necessary to halt or contain the discharge of a hazardous substance or to minimize the harmful effects of the discharge to the air, lands or waters of the state. When required, free product removal shall be conducted, to the maximum extent practicable, in compliance with all of the following requirements:

(1) Free product removal shall be conducted in a manner that minimizes the spread of

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contamination into previously uncontaminated zones using recovery and disposal techniques appropriate to the hydrologic conditions at the site or facility, and that properly reuses or treats discharges of recovery byproducts in compliance with applicable state and federal laws.

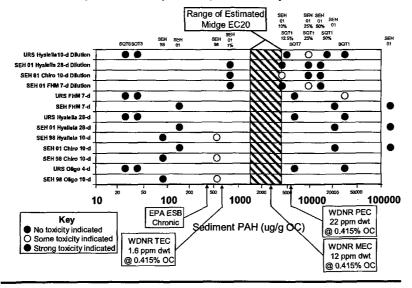
- (2) Free product removal systems shall be designed to abate free product migration.
- (3) Any flammable products shall be handled in a safe and competent manner to prevent fires or explosions.

Using the above criteria, the removal of free-product (tar) will be further refined in subsequent technical memoranda and the FS.

FIGURES

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Figure 1 -- Summary of Toxicity Data for Sandy Sediments



ATTACHMENT A ESTIMATION OF MIDGE EC20 VALUES

Because Xcel/URS were unsuccessful at completing toxicity tests with *Chironomus* during themost recent investigations, the only site-specific testing with *Chironomus* across a concentration gradient in sandy sediments was the SEH (2001) dilution study. Regression analysis of these data yielded an EC20 of 4100 ug/g OC. Because of subtle differences in the slopes of the regression line, the estimated LC20 for this study was actually slightly lower, 3760 ug PAH/g OC. Because of this, the mean of these two, 3930 ug PAH/g OC is proposed as the 20% effect level for this study. An uncertainty with this value lies with the analytical characterization which contains some irregularities as pointed out previously by Xcel/URS.

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The water-only fluoranthene data of Schuler et al. (2004) can also be used to estimate sediment effect concentrations. The reported water-only 10-d LC50 for *Chironomus* was 36 ug/L which, given the Kow and molecular weight of fluoranthene, corresponds to a predicted sediment LC50 of 3280 ug PAH/g OC. However, this value needs to be corrected from an LC50 to a 20% effect level. An estimate of this correction is available from the exposure response curve from the SEH (2001) sandy sediment dilution study, in which the ratio of the LC50 to the LC20, which is 6090/3760 or 1.62. Because the LC20 and EC20 were so close in this study, the lethality data were not adjusted downward further for sublethal effects. This results in an estimated LC20 based on the Schuler study of 2020 ug PAH/g OC.

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Another point of reference is the toxicity of SQT7 to *Hyalella azteca*; this sediment caused about-80% mortality of *Hyalella* at 6080 ug PAH/g OC. Toxicity testing of this sediment with *Chironomus* was unsuccessful. However, assuming this concentration in this sediment represents an LC80 exposure for *Hyalella*, other data can be used to estimate a response that might be expected from *Chironomus*. One way is to look at the ratio of the *Hyalella* LC80 in the SEH (2001) sandy sediment dilution test to the *Chironomus* effect threshold mentioned above. This would be a ratio of 17800/3930 or 4.53. Dividing the PAH concentration in SQT7 by this value yields 6080/4.53 or 1342 ug PAH/g OC. Another way would be to adjust from a *Hyalella* LC80 to a *Hyallela* LC50 using the ratios of those values from the SEH (1.24) and URS (1.34; geo mean = 1.29), adjust to a *Chironomus* LC50 based on the ratio from Schuler (59/36 = 1.64) and to a *Chironomus* LC20 based on SHE (2001) as above (1.62). This gives an estimated *Chironomus* LC20 of 6080/(1.29*1.64*1.62) = 1770 ug PAH/g OC.

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A final method would be to estimate the *Chironomus* LC20 based on the URS (2006) sandy-sediment dilution test with *Hyalella*, which gave a 10-d LC50 of 12700 ug PAH/g OC. This can be adjusted to an estimated *Chironomus* 10-d LC50 using the Schuler data (110/36 = 3.06) and to an LC20 based on SEH (2001; 1.62). This yields an estimated *Chironomus* 10-d LC20 of 12700/(3.06*1.62) = 2560 ug PAH/g OC.

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Attachment 1
Sediment Chemistry Data from URS 2005 BERA

			тос тос		PARTICLE SIZE ANALYSIS OF SEDIMENTS							
	TPAH	тос		TPAH NOC	% Solids	Non-Soil Mass	Gravel				Silt & Clay Fines %	% S&C Fines
Sample ID#, Date of Collection	(dw ug/kg)	(dw mg/kg)	(%)	(ug/g OC)		%	Size %	Size %	Size %	Size %	Size (<p200)< th=""><th>and Fine Sand</th></p200)<>	and Fine Sand
SQT 1, sandy site, June 2005				, , , , , , , , , , , , , , , , , , ,								
SQT1 Mean of Replicates	442,595	6,196	0.6%	57,118	79	2	0.0	0.5	32	60	8	68
Standard Deviation +/-	487,715	3,524	0.4%	42,721	2	4	0.1	0.3	4	5	5	3
Median	260,275	4,950	0.5%	70,155	79	1	0.0	0.6	32	60	9	68
SQT 1 Composite Grab (TPAH avg with dup)	376,815	3,175	0.3%	118,682			<u> </u>]		
SQT Tox Test Homogenized Sample	166,940	4,600	0.5%	36,291	İ		İ					
SQT 2, woody site, June 2005								, ,				
SQT 2 Mean of Replicates	3,545	427,400	42.7%	9	37	82	0.0	0.0	32	45	24	69
Standard Deviation +/-	1,314	139,292	13.9%	3	5	30	0.0	0.1	13	12	22	11
Median	3,283	385,000	38.5%	8	37	79	0.0	0.0	33	48	19	67
SQT 2 Composite Grab	4,815	100,000	10.0%	48	0,	,,	0.0	0.0		10	13	67
SQT Tox Test Homogenized Sample	3,195	420,000	42.0%	8								
SQT 3, woody site, June 2005	0,190	720,000	42.070	<u> </u>						 		
SQT 3 Mean of Replicates	21,989	294,400	29.4%	68	35	52	0.0	0.0	9	53	38	91
l '	14,228	140,190	14.0%	19	10	32	0.0	0.0	3	16		91
Standard Deviation +/-			14.0% 36.4%	69	34	41	0.0	0.0	8	47	17	4
Median	25,235	364,000	36.4% 13.7%		34	41	0.0	0.0	°	4/	48	92
SQT 3 Composite Grab (TPAH avg with dup)	21,270	136,500		156 43]		
SQT Tox Test Homogenized Sample	17,060	400,000	40.0%	43						 		
SQT 4, woody site, June 2005	00,000	400.004	40.00/	50	20	161	ا م	0.0	00		99	70
SQT 4 Mean of Replicates	20,302	420,201	42.0%	56	29		0.0	0.0	22	50	28	78
Standard Deviation +/-	6,214	120,013	12.0%	36	2	58	0.0	0.0	8	13	18	8
Median	19,390	461,000	46.1%	42	30	146	0.0	0.0	24	52	24	<i>76</i>
SQT 4 Composite Grab	26,942	160,000	16.0%	168								
SQT Tox Test Homogenized Sample	14,098	420,000	42.0%	34								
SQT 5, woody site, June 2005												
SQT 5 Mean of Replicates	57,462	348,600	34.9%	172	31	75	0.0	0.0	23	46	31	77
Standard Deviation +/-	17,101	135,253	13.5%	34	3	. 12	0.0	0.0	8	6	13	8
Median	54,500	363,000	36.3%	157	31	74	0.0	0.0	23	46	35	77
SQT 5 Composite Grab (TPAH avg with dup)	84,003	265,500	26.6%	316						1		
SQT Tox Test Homogenized Sample	31,250	250,000	25.0%	125								
SQT 6, sandy site, June 2005												
SQT 6 Mean of Replicates	4,155	79,060	7.9%	52	36	8	0.0	0.0	4	22	74	96
Standard Deviation +/-	1,879	15,550	1.6%	15	2	5	0.0	0.0	1	6	6	1
Median	3,505	82,900	8.3%	48	36	7	0.0	0.0	4	20	76	96
SQT 6 Composite Grab	9,038	14,000	1.4%	646						İ		
SQT Tox Test Homogenized Sample	2,297	95,000	9.5%	24								
SQT 7, sandy site, June 2005												
SQT 7 Mean of Replicates	21,209	2,352	0.2%	16,148	78	2	0.2	0.7	36	59	4	63
Standard Deviation +/-	25,828	1,078	0.1%	26,426	3	2	0.4	0.4	1	2	2	1
Median	13,720	2,190	0.2%	4,314	<i>7</i> 8	1	0.0	0.6	36	59	4	63
SQT 7 Composite Grab (TPAH avg with dup)	14,058	3,100	0.3%	4,535								
SQT Tox Test Homog Sample (avg TPAH with dup)	23,096	3,500	0.4%	6,599						Ì		
SQT 8, woody site, June 2005		· · · · · · · · · · · · · · · · · · ·		<u> </u>								
SQT 8 Mean of Replicates	116,331	290,840	29.1%	288	36	70	14.4	0.3	24	48	14	62
Standard Deviation +/-	161,989	179,095	17.9%	344	12	71	13.3	0.5	7	6	11	14
Median	86,630	309,000	30.9%	182	33	52	21.9	0.2	23	51	16	63
SQT 8 Composite Grab	124,238	42,000	4.2%	2,958		\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \				·	,,	03
SQT Tox Test Homog Sample (TPAH Avg with Dup)	59,137	385,000	38.5%	154		:				1		
OUT TOX TEST MORROY Sample (TPAH AVG WITH DUP)	33,137	202,000	30.370	1.54	<u> </u>			·	· <u>·</u>		<u></u>	

Attachment 1
Sediment Chemistry Data from URS 2005 BERA

	<u> </u>			T	PARTICLE SIZE ANALYSIS OF SEDIMENTS							
	TPAH	TOC	TOC	TPAH NOC	% Solids	Non-Soil Mass	Gravel	Coarse Sand	Medium Sand		Silt & Clay Fines %	% S&C Fines
Sample ID#, Date of Collection	(dw ug/kg)	(dw mg/kg)	(%)	(ug/g OC)		%	Size %	Size %	Size %	Size %	Size (<p200)< th=""><th>and Fine Sand</th></p200)<>	and Fine Sand
SQT 9, Reference woody site, June 2005		<u> </u>	· · · · · · · · · · · · · · · · · · ·]
SQT 9 Mean of Replicates	426	20,808	2.1%	35	55	11	0.0	0.3	21	75	4	80
Standard Deviation +/-	-	23,103	2.3%	17	9	8	0.0	0.2	3	7	4	4
Median	426	10,500	1.1%	41	58	7	0.0	0.3	21	73	4	80
SQT 9 Composite Grab	334	32,000	3.2%	10						}		
SQT Tox Test Homogenized Sample	83	58,000	5.8%	1	, ,							
SQT 10, Reference sandy site, June 2005												
SQT 10 Mean of Replicates	426	4,320	0.4%	140	74	1	0.0	0.2	10	87	3	90
Standard Deviation +/-	-	3,905	0.4%	58	3	1	0.0	0.1	4	4	3	4
Median	426	2,600	0.3%	164	72	1	0.0	0.2	9	89	2	91
SQT 10 Composite Grab (TPAH avg with Dup)	230	860	0.1%	268				ł				
SQT Tox Test Homogenized Sample	26	1,300	0.1%	20						·		
SQT 11, Reference woody site, June 2005	:		<u> </u>									
SQT 11 Mean of Replicates	9,856	502,600	50.3%	20	29	131	0.0	0.0	25	48	29	76
Standard Deviation +/-	12,611	80,996	8.1%	25	4	50	0.0	0.0	7	23	19	8
Median	4,260	499,000	49.9%	10	29	129	0.0	0.0	22	37	31	78
SQT 11 Composite Grab	740	78,000	7.8%	9								
SQT Tox Test Homogenized Sample	3,798	280,000	28.0%	14								
SQT 12, Reference sandy site, June 2005		·		T								
SQT 12 Mean of Replicates	1,106	869	0.1%	1,264	74	0	0.2	0.0	1.3	96	3	99
Standard Deviation +/-	<i>570</i>	<i>55</i>	0.0%	605	1	0	0.2	0.0	0.3	2	1	0
Median .	852	872	0.1%	990	74	-	0.0	0.0	1.2	96	3	99
SQT 12 Composite Grab (TPAH avg with dup)	435	407	0.0%	1,069			İ		<u> </u>			
SQT Tox Test Homogenized Sample	8	320	0.0%	26								
SQT 13, Reference sandy site, September 2005										1	_	
SQT 13 Mean of Replicates	426	2,742	0.3%	157	69		0.0	0.0	0.8	94	5	99
Standard Deviation +/-	-	268	0.0%	15	1	-	0.0	0.0	0.1	1	1	0
Median	426	2,750	0.3%	155	70		0.0	0.0	0.8	94	5	99
SQT 13 Composite Grab (TPAH avg with dup)	224	2,460	0.2%	91								
SQT Tox Test Homogenized Sample	NO DATA PROVID	ED								ļ	·	
SQT 14, Reference sandy site, September 2005							ļ	ļ			_	
SQT 14 Mean of Replicates	426	3,866	0.4%	113	73	-	0.6	0.4	12	80	7	87
Standard Deviation +/-	-	665	0.1%	18		-	0.5	0.1	2	2	1	2
Median	426	3,820	0.4%	120	74		0.4	0.5	13	80	7	87
SQT 14 Composite Grab (TPAH avg with dup)	67	2,800	0.3%	24						1		
SQT Tox Test Homogenized Sample	NO DATA PROVID	ED			Ĺ I		1			<u> </u>		<u> </u>

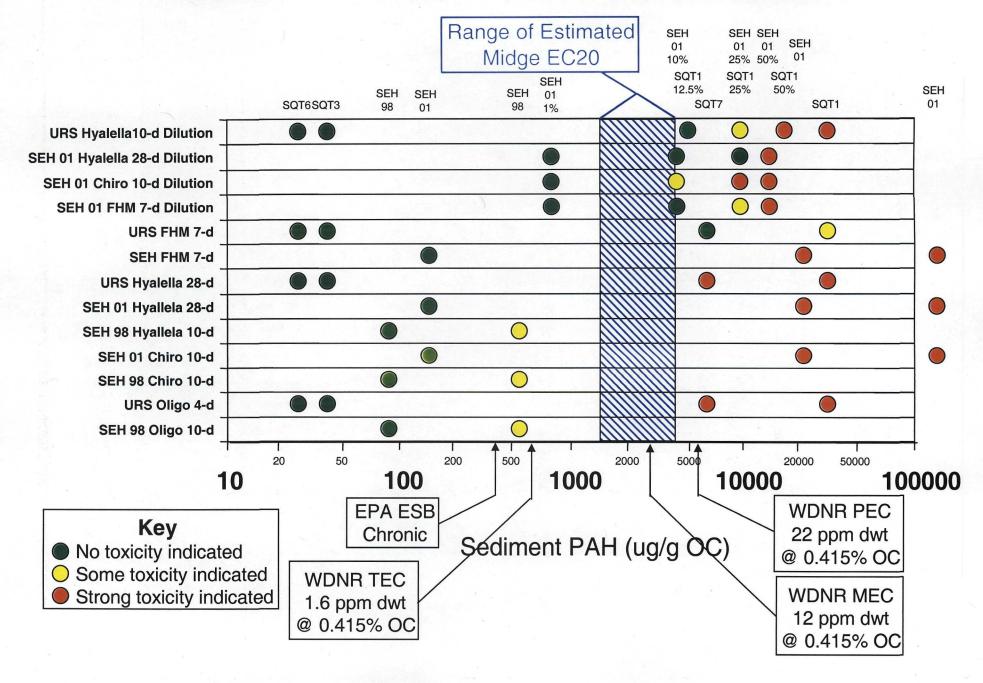
Attachment 1
Sediment Chemistry Data from URS 2005 BERA

				T	1			PARTICI E SIZI	E ANALYSIS OF	SEDIMENTS		
	TPAH	тос	тос	TPAH NOC	% Solids	Non-Soil Mass	Gravel	Coarse Sand	Medium Sand		Silt & Clay Fines %	% S&C Fines
Sample ID#, Date of Collection	(dw ug/kg)	(dw mg/kg)	(%)	(ug/g OC)	/	%	Size %	Size %	Size %	Size %	Size (<p200)< th=""><th>and Fine Sand</th></p200)<>	and Fine Sand
SQT 1, sandy site, June 2005	(=1, =3,3)	(<u>ug</u> , <u>g</u> /		(5.5.5.7				<u> </u>		<u> </u>	0.120 (4. 200)	and in our
SQT1 Mean of Replicates	442,595	6,196	0.6%	57,118	79	2	0.0	0.5	32	60	8	68
Standard Deviation +/-	487,715	3,524	0.4%	42,721	2	4	0.1	0.3	4	5	5	3
Median	260,275	4,950	0.5%	70,155	79	1	0.0	0.6	32	60	q	68
SQT 1 Composite Grab (TPAH avg with dup)	376,815	3,175	0.3%	118,682		·	5.0	1	-		V]
SQT Tox Test Homogenized Sample	166,940	4,600	0.5%	36,291	ĺ					1		ĺ
SQT 2, woody site, June 2005	100,0 10	4,000	0.070	00,201					······································			
SQT 2 Mean of Replicates	3,545	427,400	42.7%	9	37	82	0.0	0.0	32	45	24	69
Standard Deviation +/-	1,314	139,292	13.9%	3	5	30	0.0	0.1	13	12	22	11
	3,283	385,000	<i>38.5%</i>	8	37	79	0.0	0.0	33	48	19	67
Median	4,815	100,000	<i>38.5 %</i> 10.0%	48	. 3/	79	0.0	0.0	33	40	19	67
SQT 2 Composite Grab	· ·		42.0%	8				1				
SQT Tox Test Homogenized Sample	3,195	420,000	42.0%	 					<u> </u>			
SQT 3, woody site, June 2005	04.000	004.400	00.49/	68	35	52	0.0	۸,	9	F0	00	
SQT 3 Mean of Replicates	21,989	294,400	29.4%	1	, ,		0.0	0.0	9	53	38	91
Standard Deviation +/-	14,228	140,190	14.0%	19	10	32	0.0	0.0	4	16	17	4
Median .	25,235	364,000	36.4%	69	34	41	0.0	0.0	8	47	48	92
SQT 3 Composite Grab (TPAH avg with dup)	21,270	136,500	13.7%	156	1							
SQT Tox Test Homogenized Sample	17,060	400,000	40.0%	43						<u> </u>		
SQT 4, woody site, June 2005										_		
SQT 4 Mean of Replicates	20,302	420,201	42.0%	56	29	161	0.0	0.0	22	50	28	78
Standard Deviation +/-	6,214	120,013	12.0%	36	2	58	0.0	0.0	8	13	18	8
Median	19,390	461,000	46.1%	42	30	146	0.0	0.0	24	52	24	<i>76</i>
SQT 4 Composite Grab	26,942	160,000	16.0%	168	}					ł		
SQT Tox Test Homogenized Sample	14,098	420,000	42.0%	34		<u> </u>						
SQT 5, woody site, June 2005				1								
SQT 5 Mean of Replicates	57,462	348,600	34.9%	172	31	75	0.0	0.0	23	46	31	77
Standard Deviation +/-	17,101	135,253	13.5%	34	3	12	0.0	0.0	8	6	13	8
Median	54,500	363,000	36.3%	157	31	74	0.0	0.0	23	46	35	77
SQT 5 Composite Grab (TPAH avg with dup)	84,003	265,500	26.6%	316								
SQT Tox Test Homogenized Sample	31,250	250,000	25.0%	125								
SQT 6, sandy site, June 2005												
SQT 6 Mean of Replicates	4,155	79,060	7.9%	52	36	8	0.0	0.0	4	22	74	96
Standard Deviation +/-	1,879	15,550	1.6%	15	2	5	0.0	0.0	1	6	6	1
Median	3,505	82,900	8.3%	48	36	7	0.0	0.0	4	20	76	96
SQT 6 Composite Grab	9,038	14,000	1.4%	646	1					ı İ		
SQT Tox Test Homogenized Sample	2,297	95,000	9.5%	24	ļ	!			l	ļ	l	
SQT 7, sandy site, June 2005	 											
SQT 7 Mean of Replicates	21,209	2,352	0.2%	16,148	78	2	0.2	0.7	36	59	4	63
Standard Deviation +/-	25,828	1,078	0.1%	26,426	1	2	0.4	0.4	1	2	2	1
Median	13,720	2,190	0.2%	4,314	: :	1	0.0	0.6	36	- 59	<u> </u>	63
SQT 7 Composite Grab (TPAH avg with dup)	14,058	3,100	0.3%	4,535			*.*	-10			7	00
SQT Tox Test Homog Sample (avg TPAH with dup)	23,096	3,500	0.4%	6,599) i						ì	
SQT 8, woody site, June 2005	20,000	0,000			 							
SQT 8 Mean of Replicates	116,331	290,840	29.1%	288	36	70	14.4	0.3	24	48	14	62
	161,989	179,095	17.9%	344	12	71	13.3	0.5	2 4 7	40		
Standard Deviation +/-			17.9% 30.9%	182	33	52 52	13.3 21.9	0.5 0.2	23	51	11	14
Median	86,630	<i>309,000</i> 42,000	<i>3</i> 0.9% 4.2 %	2,958		52	21.9	<i>∪.∠</i>	23	51	16	. 63
SQT 8 Composite Grab	124,238			154		į				į		i
SQT Tox Test Homog Sample (TPAH Avg with Dup)	59,137	385,000	38.5%	104	<u> </u>							

Attachment 1
Sediment Chemistry Data from URS 2005 BERA

	T 1			1				PARTICLE SIZE	ANALYSIS OF	SEDIMENTS		
	TPAH	TOC	TOC	TPAH NOC	% Solids	Non-Soil Mass	Gravel	Coarse Sand			Silt & Clay Fines %	% S&C Fines
Sample ID#, Date of Collection	(dw ug/kg)	(dw mg/kg)	(%)	(ug/g OC)	/ / Conido	%	Size %	Size %	Size %	Size %	Size (<p200)< th=""><th>and Fine Sand</th></p200)<>	and Fine Sand
SQT 9, Reference woody site, June 2005	(<u></u>	(75)	(, ,						
SQT 9 Mean of Replicates	426	20,808	2.1%	35	55	11	0.0	0.3	21	75	4	80
Standard Deviation +/-	_	23,103	2.3%	17	9	8	0.0	0.2	3	7	4	4
Median	426	10,500	1.1%	41	58	7	0.0	0.3	21	73	4	80
SQT 9 Composite Grab	334	32,000	3.2%	10								
SQT Tox Test Homogenized Sample	83	58,000	5.8%	1	ĺ							
SQT 10, Reference sandy site, June 2005				 								·
SQT 10 Mean of Replicates	426	4,320	0.4%	140	74	1	0.0	0.2	10	87	3	90
Standard Deviation +/-	.	3,905	0.4%	58	3	1	0.0	0.1	4	4	3	4
Median	426	2,600	0.3%	164	72	1	0.0	0.2	9	89	2	91
SQT 10 Composite Grab (TPAH avg with Dup)	230	860	0.1%	268			}		j	J		ļ
SQT Tox Test Homogenized Sample	26	1,300	0.1%	20					ļ			
SQT 11, Reference woody site, June 2005		· · · · · · · · · · · · · · · · · · ·	·									
SQT 11 Mean of Replicates	9,856	502,600	50.3%	20	29	131	0.0	0.0	25	48	29	76
Standard Deviation +/-	12,611	80,996	8.1%	25	4	50	0.0	0.0	7	23	19	8
Median	4,260	499,000	49.9%	10	29	129	0.0	0.0	22	37	31	78
SQT 11 Composite Grab	740	78,000	7.8%	9			}		j	ļ	·	
SQT Tox Test Homogenized Sample	3,798	280,000	28.0%	14				· ·	1			
SQT 12, Reference sandy site, June 2005		-										
SQT 12 Mean of Replicates	1,106	869	0.1%	1,264	74	0	0.2	0.0	1.3	96	3	99
Standard Deviation +/-	570	55	0.0%	605	1	О	0.2	0.0	0.3	2	1	0
Median	852	872	0.1%	990	74	-	0.0	0.0	1.2	96	3	99
SQT 12 Composite Grab (TPAH avg with dup)	435	407	0.0%	1,069				1				
SQT Tox Test Homogenized Sample	8	320	0.0%	26			ĺ	ĺ				
SQT 13, Reference sandy site, September 2005			•									
SQT 13 Mean of Replicates	426	2,742	0.3%	157	69	-	0.0	0.0	0.8	94	5	99
Standard Deviation +/-	-	268	0.0%	15	1	-	0.0	0.0	0.1	1	1	О
Median	426	2,750	0.3%	155	70		0.0	0.0	0.8	94	5	99
SQT 13 Composite Grab (TPAH avg with dup)	224	2,460	0.2%	91				ł		1		1
SQT Tox Test Homogenized Sample	NO DATA PROVID	ED]			
SQT 14, Reference sandy site, September 2005			-									
SQT 14 Mean of Replicates	426	3,866	0.4%	113	73	-	0.6	0.4	12	80	7	87
Standard Deviation +/-	-	665	0.1%	18	3	-	0.5	0.1	2	2	1	2
Median	426	3,820	0.4%	120	74		0.4	0.5	13	80	7	87
SQT 14 Composite Grab (TPAH avg with dup)	67	2,800	0.3%	24			ĺ	[1	1
SQT Tox Test Homogenized Sample	NO DATA PROVID	ED										

Attachment 2 -- Summary of Toxicity Data for Sandy Sediments





UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

NATIONAL HEALTH & ENVIRONMENTAL EFFECTS RESEARCH LABORATORY MID-CONTINENT ECOLOGY DIVISION 6201 CONGDON BOULEVARD, DULUTH, MINNESOTA 55804

OFFICE OF RESEARCH AND DEVELOPMENT

April 5, 2007

SUBJECT: Analysis of photoactivation issue relative to Ashland BERA

FROM: David R. Mount, Research Aquatic Biologist

TO: Scott Hansen, RPM Ashland Superfund Site

The following text describes my assessment of the predicted effects of combined UV and PAH exposure at the Ashland site based on the available experimental data. A draft of this memo was reviewed by Dr. Russell Erickson; his comments were incorporated and he is in agreement with the analysis.

For short term exposure, response to UV/PAH exposure has been shown to be proportional to the product of the PAH exposure (often expressed in terms of body burden) and the UV exposure. In the case of sediment exposure without measured body burdens, the sediment PAH concentration (OC normalized) should be a reasonable surrogate for PAH dose if one assumes that the organisms came to a steady state body burden relatively quickly. The uncertainty here is on the side of leniency (i.e. the opposite of environmentally conservative) as it would underestimate effects if steady state was not achieved. Under the steady state assumption, the expression of exposure as a product of sediment PAH concentration and UV exposure should be an appropriate way to compare results among experiments.

Figures 1 and 2 show the exposure-response relationships for the URS (2006) and SEH (2001) exposures of *Hyalella* to dilutions of a sandy PAH contaminated sediment from the site, with and without UV light. The PAH concentration for the 50% dilution in the SEH study has been adjusted as suggested previously by URS. These experiments show that the addition of UV light to sediment exposure consistently increases toxicity. In the URS study, the increase in toxicity from a 24-hour average UV of 28.3 μ W/cm² (a 16-h photoperiod averaged over 24 hours) was about 2.1 fold, with the LC50 decreasing from 12750 μ g PAH/g OC to 6050 μ g PAH/g OC. In the SEH test, the average UV exposure was slightly higher (24-h average of 34.5 μ W/cm²) and the increase in toxicity was about 2.7 fold, with the LC50 decreasing from 14418 to 5351 μ g PAH/g OC. Taking into account the slightly higher UV in the SEH tests, these results are remarkably close.

One difference between the URS and SEH tests is test duration – the URS test was a 10-d test, while the SEH test was a 28-d test. Because the UV dose is cumulative and therefore increases with time of exposure, one might expect that a longer exposure would show comparable effects

at a lower PAH concentration. However, despite the difference in duration, the LC50 values expressed on the basis of sediment PAHs were remarkably close. One explanation for this similarity might be that the duration of the SEH exposure was long enough for damage repair rates to become significant. The concept that the potency of UV/PAH exposure is a linear function of PAH * UV * time assumes that accumulated damage from UV/PAH exposure is repaired at a negligible rate, which appears to be true for shorter term exposures. However, it is reasonable to expect that for less severe exposures, which create damage at a slower rate over longer periods, repair rates will become significant. Thus, it may be that LC50 concentrations become asymptotic at longer exposure periods such as 10-28 days.

A second explanation is that the PAH exposure in the URS and SEH tests differed in a way not reflected by the reported PAH concentrations in the sediment. The evidence for this explanation is that the SEH 28-d Hyalella test without supplemental UV showed lower sensitivity to PAHs (28-d LC50 14400 μ g PAH/g OC) than did the 10-d test without UV conducted by URS (10-d LC50 12700 μ g PAH/g OC). Based on literature data (e.g., Schuler et al. 2004; ES&T 38:6247), one would expect the 28-d LC50 in the absence of UV light to be about half of the 10-d LC50.

For purposes of this analysis the former explanation, that damage repair becomes significant in longer term exposures, was used. While a more lenient (as opposed to environmentally conservative) assumption, it is not excessively so, and is very consistent with what one would expect from the underlying biology. Under this assumption, one can compare the two test responses by plotting them on the same axis using average daily UV/PAH exposure ([μ W-h UV/cm²] * [μ g PAH/g OC]). Doing so is strongly suggestive of a single exposure response curve with an LC50 of 4.2 [W-h UV/cm²] * [μ g PAH/g OC] and an LC20 of 2.947 [μ W-h UV/cm²] * [μ g PAH/g OC] (Figure 5).

The two UV experiments discussed above were both conducted to simulate UV intensity at moderate depth, circa 8 feet. However, UV penetration is highly depth dependent, so much greater UV intensity can be expected at shallower depths. EPA suggested to URS/Xcel on multiple occasions that additional UV exposures should be conducted at higher UV intensities in order to quantify the expected response at shallower depths. However, URS/Xcel declined to follow EPA's suggestion, so the BERA is left to extrapolate results representing moderate depths to responses that would be expected at shallower depths.

To do this, the extinction curve determined from UV measurements at the site was used to estimate the degree of light penetration at various. The extinction equation was:

% of surface UV at x cm depth = $10^{(-0.0064*x+1.9769)}$

Based on previous calculations, the 24-h average UVA irradiance at the water's surface in June was estimated at 977 μ W/cm². The expected 24-h dose expected at any depth equals the percentage UV penetration to that depth multiplied by the surface UVA multiplied by 24 hours. This can be divided by 10⁶ to convert μ W to W. If one divides the LC20 (from the PAH/UV response regression described above) by the depth-specific 24-h UV dose just described, the

result is the sediment PAH concentration expected to result in 20% lethality to *Hyalella* at that depth. Table 1 shows the results of these calculations.

A final issue relates to the degree to which overlying debris might provide partial shading to benthic organisms living at the site. All of the exposures discussed thus far have had no shading provided aside from the test sediment itself. To explore the shading issue, URS conducted an additional series of treatments in which leaf plugs were added to the test chambers to provide shade like might be expected from a sediment surface with overlying debris. The results of this exposure series, compared to the response obtained without UV, and with UV but without shading, is shown in Figure 6. These data indicate an intermediate response by organisms exposed in the presence of leaf plugs. The presumption is that the decreased sensitivity of Hyalella to UV/PAH in the presence of leaf plugs is associated with decreased UV exposure, although no measurements were made to determine if the presence of leaf plugs might have decreased bioavailability and/or accumulation of sediment PAHs. Previous analyses conducted by Dr. Russell Erickson of EPA/ORD-Duluth (provided to Xcel as part of initial EPA comments on the draft BERA) empirically estimated the amount of shading provided by the presence of leaf plugs, based on the differential responses among treatments with no UV, and UV with and without leaf plugs. The estimate was that the presence of overlying debris (leaf plugs) reduced UV exposure by 40%. This value can be used to estimate the expected response of Hyalella in the presence of overlying debris, by recalculating the depth-specific PAH LC20 concentrations assuming 40% less UV exposure. These "with debris" values are shown along with the "no debris" LC20 values in Table 1. Selection of thresholds to apply at the site depends on the degree to which overlying debris is expected (before or after remedial action) and how the shading effect of the debris layer would relate to that used in the laboratory experiments. in this range would depend on the degree to which overlying debris is available at the site, both before and after any remedial action. Table 1 also shows these LC20 values adjusted to a dry weight basis, assuming an organic carbon content of 0.415%, the average of the OC content in SQT1 and SQT7.

The extrapolation to UV exposures expected in areas shallower than 8 ft presumes that the increase in UV exposure of benthic organisms will be proportional to the increase in incident UV at the sediment surface, and that the UV alone will not cause adverse effects. Because Xcel/URS declined to conduct testing at UV intensities higher than those expected in roughly 8 feet of water, any non-linearities that might occur in the real world cannot be estimated, and direct proportionality is the only reasonable assumption (i.e., if one doubles the UV, the PAH concentration corresponding to the LC20 will be cut in half). There has been some preliminary experimental work conducted at EPA's Duluth laboratory using PAH-spiked sediments and simultaneous UV exposure. This work is neither complete nor published. However, it suggests that Hyalella can withstand continuous UVA exposure to at least 290 µW/cm² (highest exposure tested) in the presence of West Bearskin sediment (no overlying debris) without apparent adverse effect, and Chironomus dilutus and Lumbriculus variegatus withstood continuous UVA exposure of about 770 µW/cm² (highest exposure tested) in sediment without overlying debris. While these are preliminary data, they suggest that UVA exposure alone would not prevent colonization of sediments with higher UVA exposure, although whether there is an upper limit was not determined in these experiments.

The discussion above relied exclusively on data from UV/PAH exposures with *Hyalella azteca* as the basis for estimating effect thresholds. However, several other experiments involving UV/PAH exposure were conducted during the course of site investigations. The relationship between these other studies and the analysis above is discussed in the following paragraphs.

URS (2006) also conducted exposures of larval fathead minnows to both site sediments and simultaneous UV exposure. UV exposures used in these experiments were higher than those in the *Hyalella* exposures, intended to represent UV intensity in about 4 feet of water rather than the 8 feet assumed for the *Hyalella* exposures. In terms of sediment PAH concentration associated with effects, the fathead minnows appeared comparably sensitive as *Hyalella*. Survival in SQT7 was 38% percent, with a PAH concentration of 6084 ug/g OC. This 38% survival is about half that observed in the reference treatments, so one can view 6084 as an approximate LC50 for fathead minnows at the associated UV exposure. As described above, the LC50s for *Hyallela* were 6050 and 5351 ug/g OC. In absolute terms, this implies that fathead minnows were less sensitive than *Hyalella* to UV/PAH exposure because UV exposure was higher in the fathead minnow test. Regardless, the comparison of the fathead minnow and *Hyalella* tests suggest that fathead minnows would likely be protected by thresholds calculated based on the whole sediment exposures with *Hyalella* as shown in Table 1.

Additional experiments (SEH 1998) were conducted using organisms that were exposed UV light in clean water, after exposure to contaminated sediments without simultaneous UV. These exposures were relatively short (hours) and involved relatively high UV irradiance (circa 500 μ W/cm²). While these experiments definitely demonstrate that organisms accumulated contaminants from the sediments that could be photo-activated by UV exposure, the intense UV exposure and the absence of the shading effect of sediment (as would be available in nature) make it difficult to interpret these exposures relative to the effects one would expect under field conditions.

Finally, some UV/PAH experiments were conducted using sediment elutriates. Elutriate experiments can be challenging to interpret if actual exposures are not measured. Because experimental data are available for organisms simultaneously exposed to UV and PAH in bedded sediments, it does not appear necessary to apply data from elutriate experiments to risks associated with organisms exposed to bedded sediments. Elutriate experiments may have greater applicability to a resuspension event, though the absence of measured PAH concentrations in the elutriates make it difficult to directly relate the PAH exposure occurring in the elutriate experiments to concentrations of PAHs that might occur in the water column at the site during a resuspension event. In addition, hydrodynamic events of sufficient magnitude to resuspend substantial amounts of sediment would likely also affect UV penetration into the water column. Additional analysis and/or data collection would be necessary to comprehensively evaluate the potential for photo-activated toxicity under a resuspension scenario.

Table 1. Sediment PAH concentrations estimated to cause 20% lethality of *Hyalella azteca* in 10 days of exposure with and without overlying debris.

Water	% of Surface	24-h Average	PAH at LC20 (ug/g OC)	0 (ug/g OC)	PAH at LC20 (ug/g dwt @ 0.415% OC))	lwt @ 0.415% OC))
(cm)	irradiance at Depth	Irradiance $(\mu W/cm^2)$	No Debris	With Debris	No Debris	With Debris
5	88.1	9.098	143	238	0.59	0.99
10	81.8	799.5	154	256	0.64	1.06
25	9.59	640.9	192	319	0.80	1.33
20	45.4	443.4	277	462	1.15	1.92
100	21.7	212.2	579	964	2.40	4.00
150	10.4	101.6	1210	2020	5.02	8.36
200	4.98	48.6	2530	4210	10.5	17.5
232	3.11	30.3	4050	6750	16.8	28.0
250	2.38	23.3	5280	8800	21.9	36.5
300	1.14	11.1	11000	18400	45.8	76.3

Figure 1 URS 2006 Sandy Dilution

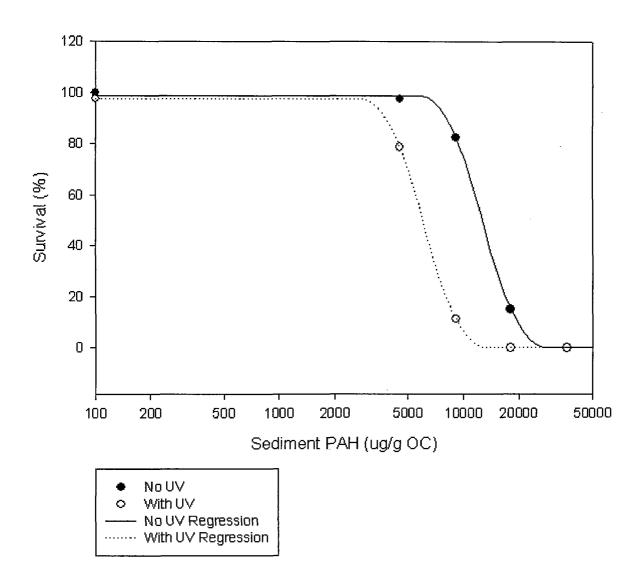


Figure 2 SEH 2001 Sandy Dilution

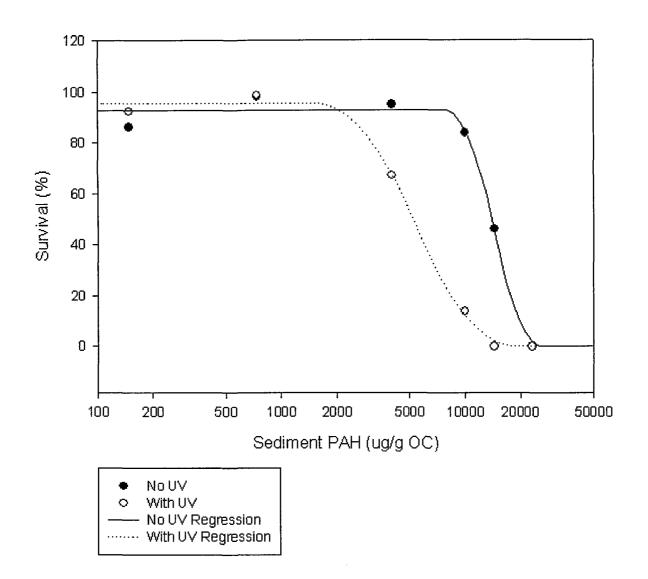


Figure 3 URS 2006 Sandy Dilution with UV

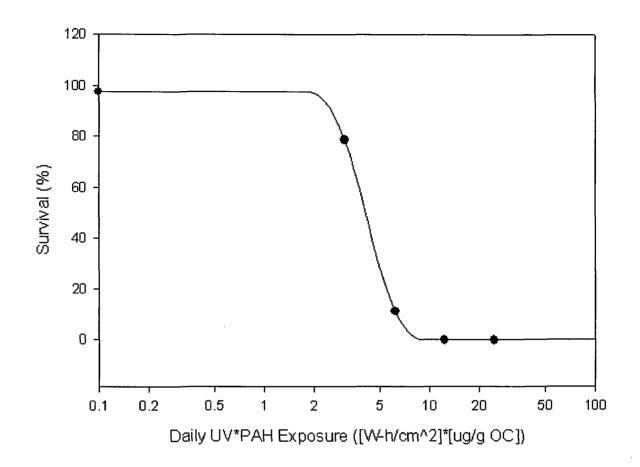


Figure 4 SEH 2001 Sandy Dilution with UV

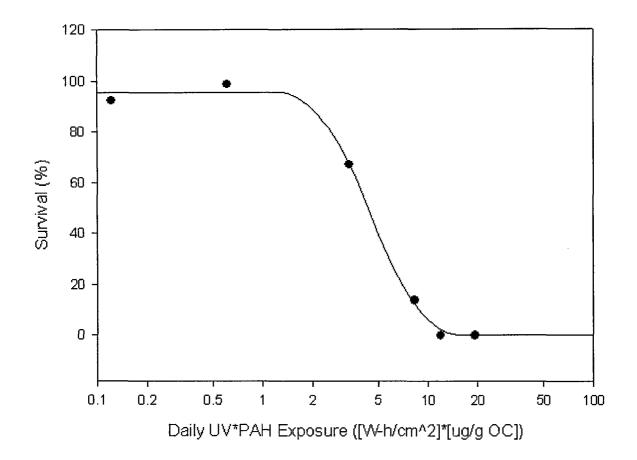


Figure 5 Combined Sandy Dilution with UV

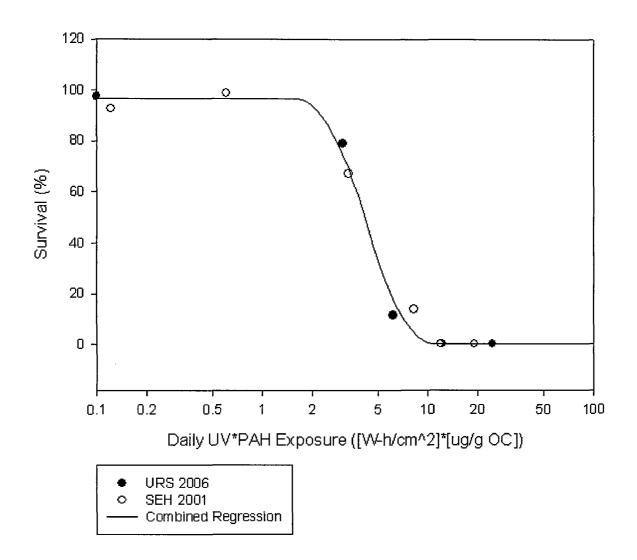
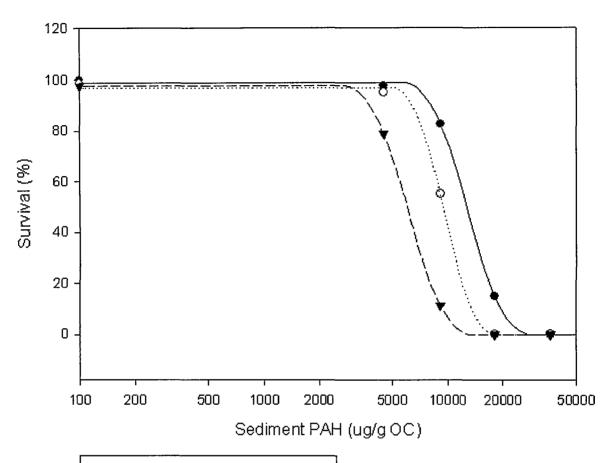


Figure 6 URS 2006 Sandy Dilution



- No UV
- UV with Leaves
- ▼ UV with No Leaves
 - No UV Regression
 - UV with Leaves Regression
- --- UV without Leaves Regression

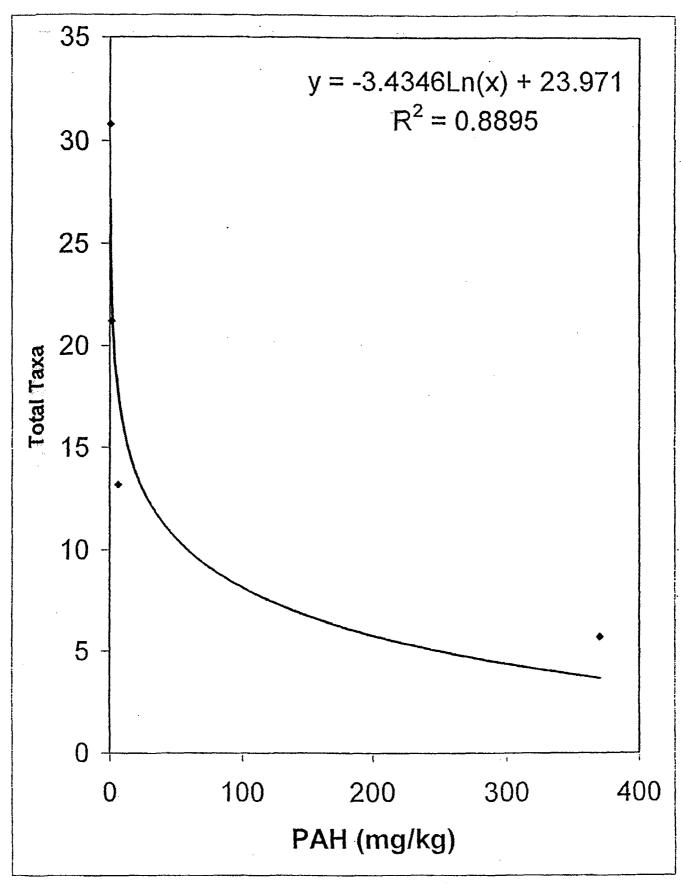
A statistical analyses was done on the paired sampling results from each substrate to determine if the results were significantly different. Separate t-tests (alpha less than or equal to 0.05) were run to compare the raw data from the two sand sites and the two wood sites. Data were transformed when necessary to achieve normality and equal variance by using natural log or natural log (x + 1) (if zero values were present in the data). Normality was tested using the Kolmogorov-Smirnov Test (with Lilliefors' correction), while equal variance was tested using the Levene Medial Test. If normality or equal variance could not be achieved, a Mann-Whitney Rank Sum Test was used. All tests were done using SigmaStat (Jandel Scientific, San Rafael, CA.). The paired results that were shown to be statistically different and the level of significance are shown in the table below. The eight indices that are significantly different in the table below are the same eight identified in the table above through qualitative means that were related to probable impacts from the coal tar contamination.. The statistical analyses confirms the conclusions reached through the qualitative evaluation of the data.



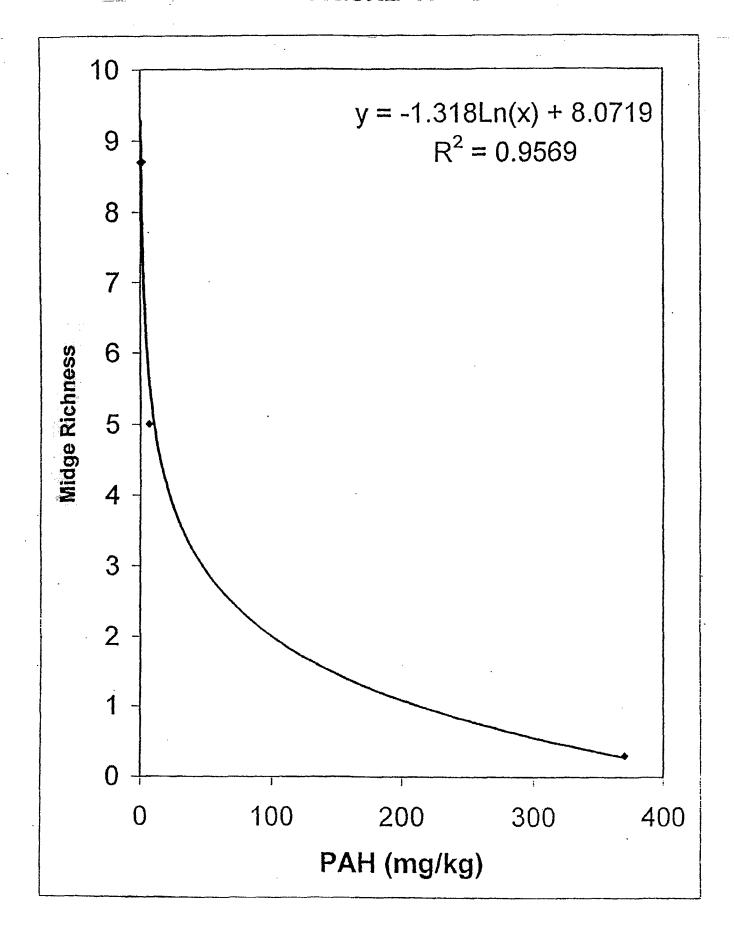
Indices	Comparison of RW:CW In		Comparison of RS:CS Index Means Level of Significance			
Total Taxa Richness	Significant	p = 0.019	Significant	p = 0.004		
Midge Taxa Richness	Significant	p = 0.002	Significant .	p = 0.007		
Total Abundance (m2)	Not significantly different	p = 0.838	Significant	p < 0.001		
Midge Abundance (m2)	Significant	p = 0.002	Significant	p < 0.001		
Oligochaete Abundance (m2)	Indance (m2) Not significantly different due to high variability at contaminated site		Significant	p < 0.001		

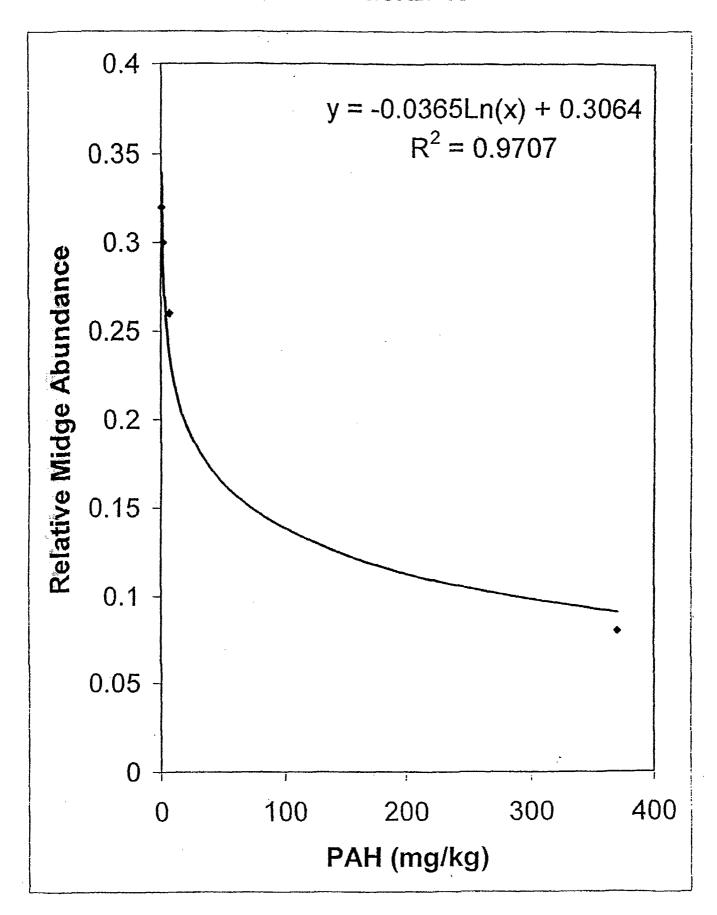
The end results of the above comparisons is the identification of four additional indices from the four identified by D & M which show probable impacts when the reference site results are compared to the contaminated site results on a qualitative and quantitative statistical basis. The above results also generally coincide with the SEH ERA qualitative analysis of the macroinvertebrate data as shown in Table 15 of the ERA.

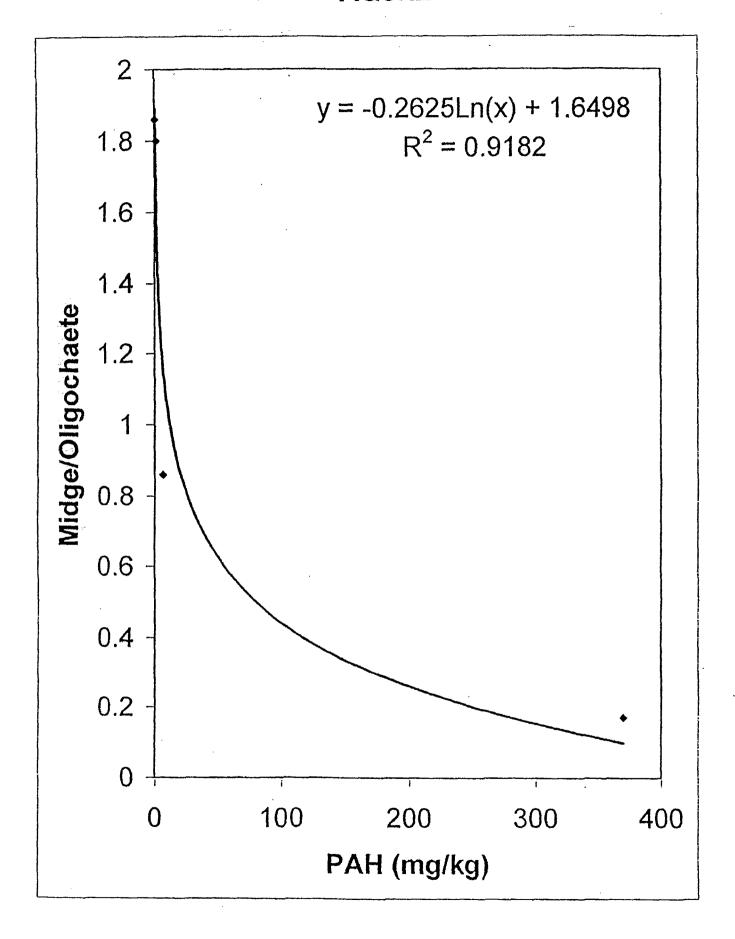
Source: WDNR (Ton JANISCH)
1999 commerts to
D&M 1999 ERA



Source D&M March 1, 1999 ERA









UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

NATIONAL HEALTH & ENVIRONMENTAL EFFECTS RESEARCH LABORATORY MID-CONTINENT ECOLOGY DIVISION 6201 CONGDON BOULEVARD, DULUTH, MINNESOTA 55804

OFFICE OF RESEARCH AND DEVELOPMENT

March 26, 2007

SUBJECT: Discussion of PAH toxicity thresholds for Ashland site sediments

FROM: David R. Mount, Research Aquatic Biologist

TO: Scott Hansen, RPM Ashland Superfund Site

I am writing to summarize my thoughts on establishing effect thresholds for PAH toxicity to benthic organisms from bedded sediments at the Ashland site. As you are aware from the recent string of written and telephone communications, the nature of the available data do not allow establishment of an effects threshold that is without uncertainty. Three major factors are responsible for this:

- 1) Not all studies targeting similar responses find the exact same exposure response profile;
- 2) Not all species tested have the same sensitivity;
- 3) While several studies have been completed, there remains a substantial gap in the toxicological information for a critical range of PAH concentrations, primarily 600 to 6000 μg/g organic carbon.

Xcel/URS have proposed a concentration of 53 ug total PAH/g¹ dwt as delineating sediments that have sufficient potential for adverse effect to require active remediation. From conversations with you, you have indicated that the remedial action objective (RAO) relative to protection of the benthic community should be a concentration expected to protect not just a single benthic organism, but the suite of benthic organisms evaluated. This is, of course, completely consistent with other regulatory approaches taken by the Agency; ecological protection is generally based on protecting most, if not all species, not just one. With this in mind, the RAO proposed by Xcel/URS fall short of your stated goals in two broad ways:

1) An analysis of the available toxicity data, along with literature data, makes clear that toxicity due to the mixture of site PAHs can be expected well below 5300 μ g/g OC, the value from which the RAO of 53 μ g/g was derived.

¹Unless otherwise noted, the term "total PAH" in this document refers to the sum of the PAH structures measured by URS in their analyses supporting the BERA. Note that a true measured of "total PAH" would include additional structures not quantified by URS in routine analyses.

The 1% organic carbon content used by Xcel/URS to convert the purported effect "threshold" of 5300 μ g/g OC to the RAO of 53 μ g/g dwt is not reflective of the organic carbon content in the sediments which were the primary determinants of that threshold (0.37% and 0.46%). This has the effect of raising the proposed RAO (expressed on a dry weight basis) by a factor of 2.4-fold above the exposures actually shown to cause the effects Xcel/URS concedes are unacceptable.

In the paragraphs that follow, I will discuss in detail why these two issues are critical, and how they can be more appropriately addressed. I will deal with the second issue first, as it is somewhat less complicated.

Translation Between Organic Carbon and Dry Weight Normalized Concentrations

The overwhelming evidence from the scientific literature shows clearly that partitioning to organic carbon (OC) controls the bioavailability, and therefore toxicity, of non-polar organic chemicals such as PAHs. For this reason, concentrations of PAHs in sediment are generally normalized on the basis of organic carbon for purposes of ecological risk assessment, as they are in the draft BERA. For this reasons, two sediments with the same dry weight (dwt) normalized PAH concentration may have pose greatly different ecological risks if their OC contents differ. However, there is often a preference on the part of remedial engineers and others to express remedial goals on a dwt basis rather than an OC basis. While this is contrary to toxicological theory, it is a practical reality, so a conversion is necessary.

This is a particularly important issue for the Ashland site, because the organic carbon contents of site sediments vary by more than a factor of 100-fold, from less that 0.4% to over 40%. This is further complicated by the belief that in sediments with relatively higher OC content, the OC is dominated by comparatively undegraded woody material, which can be suspected to have a lower affinity (i.e., lower partition coefficient) for PAHs than the more typical diagenic organic carbon likely to comprise the OC fraction in sandy, low OC sediments. If the partition coefficient for woody debris is in fact lower than that for diagenic carbon (and there is some evidence for this in the URS bioaccumulation studies and the SEH toxicity studies), then a different exposure/response relationship would be needed to determine the RAO for woody sediments. In discussions with Xcel/URS, it was proposed by Xcel/URS that a single, dwt-based RAO be developed based on responses in sandy sediment, and the same value would then be used for both sandy and woody sediments. Based on my review of the available data, I believe that establishing the RAO based on dwt-normalized concentrations in sandy sediments would in fact be protective of organisms in woody sediments if the same dwt-based RAO was applied.

Xcel/URS proposed an RAO of 53 μ g total PAH/g dwt (total PAH being defined as the total of the PAH structures URS measured in their investigations), which was derived from a value of 5300 μ g/g OC converted to a dwt basis assuming a OC content of 1%. The problem with this conversion is that the sediments that were primary drivers for the establishment of this threshold (SQT1 and SQT7) had organic carbon content well below 1% (0.46% and 0.37%, respectively). In fact, sediment SQT7, which was egregiously toxic to both *Hyalella* and *Lumbriculus*, had a dwt normalized PAH concentration of only 22.5 μ g/g dwt. According to the RAO proposed by

Xcel/URS (53 μ g/g dwt), SQT7 would not warrant active remediation, being less than half the RAO concentration, even though it was highly toxic to all species tested. Clearly, this is not consistent with a goal of protecting the suite of organisms evaluated in the BERA.

Because of this problem, the conversion of an OC-normalized threshold to a dwt-normalized RAO must consider the likely OC content to which the RAO will apply, not just a generic conversion assuming 1% organic carbon. Sampling by URS of sandy sediments both on and off site clearly indicate OC contents well below 1%. Later in this memo I will provide recommendations for dwt-normalized thresholds. For this purpose, I will use the mean of the OC measured in SQT1 and SQT7, which is 0.415%. Whether this is the exact value that should be used probably warrants further evaluation, though it is clear that something lower than 1% is necessary to accurately reflect the toxicity of sandy site sediments.

Summary: To protect benthos in sediment with the organic carbon content found in sandy site sediments collected and studied by Xcel/URS, conversion of OC-normalized PAH concentrations to dwt-normalized concentrations will require a conversion factor much lower than 1% organic carbon. This factor alone will result in an RAO much lower than the 53 μ g/g dwt proposed by Xcel/URS.

Protectiveness of a sediment PAH concentration of 5300 µg/g OC

A variety of studies were conducted in support of the Ashland BERA to assess the likely effects of different PAH concentrations in site sediments. The majority of this evidence stems from laboratory exposures of organisms to site sediments. Xcel/URS evaluated these data and proposed a value of $5300~\mu g$ PAH/g OC as delineating PAH concentrations with do or don't pose unacceptable risk to benthos. This value seems to be derived through a geometric mean of purported NOEC and LOEC values from a mixture of sediment toxicity studies with *Hyalella azteca*.

There are several aspects of the available data that argue that this value does not have the characteristics of an effect/no effect threshold for benthos. Of the sandy site sediments tested, the sediment with the closest PAH concentration to this proposed RAO is SQT7, with a PAH concentration of 6084 µg total PAH/g OC². This sediment caused >80% mortality of *Hyalella* in a 28-d exposure, and complete mortality of *Lumbriculus variegatus* in a 4-day exposure. Suggesting an RAO that is only 13% lower than a concentration causing egregious toxicity to every benthic organism tested is not consistent with a conceptual goal of little or no toxicity to benthos. URS has suggested that toxicity observed in simultaneous reference sediments reduces confidence in the finding of toxicity to *Hyalella* in SQT7, but the finding of toxicity to *Hyalella* at this PAH concentration is consistent with literature data (discussed further below).

²After the analysis supporting this memo was completed, I was informed by URS that there had been an error in calculating the total PAH values for the SQT samples reported in the URS BERA. Because this error was reported so late, a decision was made to complete this memo using the PAH values previously reported by URS. Although specific values reported in this document would be affected by this error, the overall conclusions would not be greatly affected, hence the decision to proceed based on the values originally reported.

Furthermore, this contention is irrelevant with regard to *Lumbriculus*, to which SQT 7 was highly toxic, as results from the URS bioaccumulation experiment did not indicate that there was extraneous toxicity to *Lumbriculus* in the sandy reference stations.

Equally, or perhaps more significant, is that the Xcel/URS proposed RAO does not provide protection for the midge, *Chironomus dilutus*, for which sediment toxicity data were also available. URS did not succeed in completing toxicity tests on SQT7 or other sediments with midge. However, tests of diluted site sediments conducted by SEH 2001 indicated a EC20 for midge of 4100 μ g/g OC. This value is not only lower than the proposed RAO, but was obtained using a dilution series that showed substantially lower toxicity to *Hyalella* than was found by URS in SQT7 and dilutions of SQT1, suggesting that toxicity of those sediments to midge would likely have occurred at even lower concentrations. This suggests strongly that 5310 μ g/g OC is not a concentration that would protect against toxicity to *Chironomus dilutus*.

Summary: The site-specific toxicity data, including those collected by Xcel/URS, indicate strongly that an RAO of 5300 μ g/g OC would allow for substantial sediment toxicity to all three benthic species tested in this investigation. This does not meet your definition of an appropriately protective value.

Relationship of Site Toxicity Data to Other Information on PAH Toxicity to Benthos

Among other issues, the approach taken by Xcel/URS in the draft BERA was highly empirical and did little to incorporate the larger body of knowledge of PAH effects on benthos. This is a particularly critical issue, because the available data suggest that the threshold for toxicity to benthos likes somewhere in the range of 600 to 6000 μ g/g OC, but there are very, very few sitespecific data for this concentration range. Thus, it is logical to relate the site specific responses observed in site sediments other information. If there is concordance, then these other sources of information can be used to supplement the site-specific information and, in doing so, provide a stronger basis for deriving an appropriately protective threshold.

Equilibrium partitioning (EqP), as described in the EPA ESB document for PAH mixtures, provides a mechanistic for understanding and predicting the toxicity of PAHs in sediments to benthic organisms. To apply this approach, one must assume or derive an organic carbon partition coefficient (Koc) to describe the distribution of PAH between the solid phase and interstitial water. Because it describes the relative chemical activity of PAHs in the solid phase and interstitial water, Koc is also used to quantify the bioavailability of PAHs in sediments. Although EqP can be applied regardless of the site-specific Koc value, the default approach is to assume that Koc is similar to Kow (log Koc = 0.983*Kow + 0.00028). Because Koc and Kow are nearly equal in value in the default case, it also follows that at steady state, an organism that does not metabolize PAHs will have a body burden (normalized to body lipid) that is roughly equivalent to the OC-normalized PAH concentration in sediment. Thus, the ratio of concentration in organism lipid to concentration in sediment OC (called the Biota Sediment Accumulation Factor or BSAF) is expected to be approximately one if Koc and Kow are similar, thus indicating the default EqP scenario is applicable. This same approach was used in a different context by Xcel/URS in their draft BERA.

The BSAFs for Ashland site sediments can be calculated from the bioaccumulation experiments conducted by URS using *Lumbriculus variegatus*. BSAFs calculated based on total PAH are in the range of 3 to 5 for most stations, indicating that PAH bioavailability in these sediments was, if anything, slightly higher than would be expected if Kow≈Koc. One site, SQT3 showed a much higher BSAF (10) and one site showed a much lower value (0.15). Values much higher than 1 indicate higher than expected bioavailability, which is not inconsistent with the presence of relatively undegraded wood debris, which is common at the site and is consistent with the relatively high OC content of these sediments. A value much lower than 1 indicates a higher Koc value as might result from the presence of large amounts of coal or soot. No values were obtained for SQT1 or SQT7 because these sediments were directly toxic to *Lumbriculus*. However, taken as a whole these BSAF data indicate that the assumption that Kow≈Koc is not unreasonable and is, if anything, perhaps somewhat lenient (i.e., the opposite of environmentally conservative).

The other assumption that is necessary to apply EqP theory to PAH toxicity at the Ashland site is the ratio between the concentration of all PAHs present (hundreds of structures), and those that were actually quantified for the BERA (26 structures). In the EPA ESB document, there is a recommendation that a set of 34 PAHs and PAH homolog series be considered as representing the total PAH concentration for purposes of the ESB. Data relevant to this ratio was collected in the so-called, "forensic study," which included both the 26 structures measured in the URS SQT studies, and the 34 groups in the EPA ESB recommendation. While this should lend itself to a straightforward calculation, there are irregularities in those data that reduce confidence in the calculations. For example, the sum of the two individually-measured methylnaphthalene compounds are significantly greater than the concentration reported for C1-naphthalenes; these concentrations should be equal. As a result, the correction factor for unmeasured PAHs in the BERA has some uncertainty about it which is beyond the scope of this document to fully discuss. For current purposes, a value of 1.2 was chosen, even though higher ratios were observed for other site stations, making this a lenient (as opposed to environmentally conservative) assumption. This was done because SQT1 and SQT7: 1) represent comparatively unweathered material; 2) appear to be free of woody debris and the uncertainties associated with that material (e.g., retenes); and 3) are the sites whose toxicity was central to the derivation of the RAO based on data for SQT1 and SQT7, the two most toxic samples among the SQT stations, and therefore the samples among the SQT stations that have greatest influence on the RAO. Nonetheless, this value of 1.2 is toward the low end of values reported in the literature for coal tar sites (see Hawthorne et al. 2006) and may be an assumption worthy of further evaluation.

Accepting the assumption that Kow≈Koc, and a total PAH adjustment factor of 1.2, one can use water only toxicity data for PAHs to estimate the concentrations in sediment that would be toxic to *Hyalella azteca* and *Chironomus dilutus*. Schuler et al (2004; ES&T 38:6247) published water only toxicity data for fluoranthene, reporting a water only LC50 for *Hyalella* of 110 μ g/l and 59 μ g/L for 10-d and 28-d of exposure, respectively, and the 10-d LC50 for *Chironomus dilutus* of 36 μ g/L. Assuming a middle-range Koc (5.00) and MW (202) as is represented by fluoranthene, and 1.2 as the adjustment factor for unmeasured PAHs, one would predict that the corresponding LC50's in Ashland sediments would be 10035 μ g/g OC for 10-d *Hyalella*, 5383 μ g/g OC for 28-d *Hyalella*. These values agree very well with measured responses by Hyalella to SQT1 (10-d LC50 of 12,700 μ g/g OC) and SQT7 (28-d mortality of greater than 80% at 6084 μ g/g OC).

which indicates that the assumptions of the EqP approach are appropriate for these sediments. The calculated 10-d LC50 for midge, 3284 μ g/g OC, is a little more than half of the EC50 of 6220 μ g/g OC observed in the 10-d sandy sediment dilution study with midge (SEH 2001), and the 28-d *Hyalella* LC50 from the same study (14400 μ g/g OC) was also higher than would be predicted. However, as Xcel/URS has argued consistently, there are some irregularities in the reported organic carbon concentrations from the SEH (2001) studies which may influence this comparison.

Summary: The available data support the applicability of EqP and the EPA ESB assessment approach for predicting the toxicity of PAHs in Ashland site sediments.

Calculation of a Threshold Using the EPA ESB

The EPA ESB document contains procedures for estimating a concentration of PAHs in sediment that would protect roughly 95% of all species³ from chronic toxicity of PAHs. In the ESB calculation, the overall potency of a PAH mixture depends on the distribution of compounds present. To estimate an ESB for the Ashland site, I calculated a concentration-weighted value based on the PAH composition in SQT7 (from the forensic report) with the rationale that this site was closest to the threshold. The molar concentration of each PAH in the "EMAP34" series of PAHs, and it was multiplied by the chemical specific guideline value from the ESB document. The sum of these products was then divided by the sum of all the molar concentrations to derive an overall ESB of $668 \mu g/g$ OC (this was the mean of two replicates, 670.5 and 666.0).

To relate this value to the BERA, one has to further correct for the ratio of the PAHs measured by Xcel/URS to the "EMAP34" on which the ESB is based. As described above, the ratio I have been using is 1.2, which makes the final value 557 μ g/g OC, or 2.3 μ g/g dwt at 0.415% OC.

Summary: The EPA ESB procedure suggests a value of 557 μg PAH/g OC as protecting roughly 95% of species from chronic toxicity.

Calculation of Thresholds for Benthic Species Tested for Ashland BERA

From the available data, it appears that of the three benthic species used in sediment toxicity tests, the midge *Chironomus dilutus* (formerly *tentans*) is the most sensitive. This is supported by both the comparative toxicity in sediment dilution series tested by SEH (2001) and by the literature data for water-only toxicity of fluoranthene reported by Schuler et al (2004). Therefore, if the goal is to derive an RAO that will protect these three species, then it is the toxicity threshold for midge that will set the threshold.

The first issue is to define what the threshold will be. Statistical significance is sometimes used to define toxicity thresholds, but this can be problematic because it is defined in large part by the concentrations tested and subtleties in data variability, neither of which is relevant to the

³The ESB is based on protecting the 95% percentile of species for which there are toxicity data; it is assumed that this is roughly equivalent to 95% of all species.

expected biological effect of exposure. In recent years, greater emphasis has been placed on estimating specific levels of effect using various regression techniques. For this purpose, a 20 percent effect threshold (EC20) is often chosen. While it is difficult to establish whether this is a true "threshold" for adverse effect (i.e., all concentrations below this are "safe"), it becomes difficult to reliably estimate levels of effect lower than this. It also corresponds to a level of effect that is commonly found to be significant in toxicological testing. In selecting the EC20, it is recognized that this does not guarantee the absence of biological effect at this concentration; however, it will be presumed that levels of effect lower than this will be adequately addressed through natural attenuation of residual effects.

Within the toxicity tests conducted for the Ashland BERA, there is only one test that directly determines an EC20 for midge; that was the sandy sediment dilution test by SEH (2001). While this is in some ways to most direct method for estimating this value, this study has been criticized repeatedly by Xcel/URS because of anomalies in the analytical data that make the reported exposure concentrations somewhat uncertain. As a cross check on this value, one can use the larger body of available data, to make estimates of the midge EC20 using responses in other tests and relationships among endpoints. The details of this analysis are described in detail in Attachment A, and are summarized in Table 1 below. Estimates of the midge EC20 range from 1340 to 3930 µg PAH/g OC; converting to a dwt basis assuming a sediment OC of 0.415%, this corresponds 5.57 to 16.3 µg PAH/g dwt. Because of the uncertainties involved, it may be most appropriate to think of the midge EC20 as a range rather than a single value.

Table 1 – Summary of Midge EC20 Estimates

Concentration (µg PAH/g OC)	μg PAH/g dwt. @ 0.415% OC	Summary of Derivation
1340	5.57	Treat SQT7 as <i>Hyalella</i> 28-d LC80; adjust from <i>Hyalella</i> 28-d LC80 to midge LC20 based on SEH (2001) dilution studies
1770	7.35	Treat SQT7 as <i>Hyalella</i> 28-d LC80; adjust from <i>Hyalella</i> 28-d LC80 to <i>Hyalella</i> 28-d LC50 based on URS (2006) and SEH (2001) dilution studies; adjust to midge LC50 based on Schuler (2004); adjust from midge LC50 to midge LC20 based on SEH (2001) dilution studies.
2020	8.38	Midge LC50 predicted from Schuler (2004); adjustment from LC50 to LC20 based on SEH (2001) dilution study
2560	10.6	Hyalella 10-d LC50 from URS (2006) dilution study; adjust from Hyalella 10-d LC50 to midge LC50 based on Schuler (2004); adjust midge LC50 to midge LC20 based on SEH (2001) dilution studies.
3930	16.3	Average of LC20 and EC20 from SEH (2001) test with dilutions of contaminated sandy sediment.

Note that these values are still not as low as the calculated EPA ESB concentration of $557 \,\mu g$ PAH/g OC (2.31 $\,\mu g$ PAH/g dwt at 0.415% OC). Among the reasons for this is that the EC20 midge is the lowest value from among three species, and would not necessarily protect even more sensitive species. Basing an RAO on the midge EC20 should be done in recognition that effects to highly sensitive organisms are possible, and may require additional attenuation of exposure over time to meet a more stringent definition of "threshold."

Summary: Based on a variety of data sources, the EC20 for midge is expected to lie within a range of 1340 to 3930 μ g PAH/g OC. At an OC of 0.415%, this corresponds to 5.6 to 16.3 μ g PAH/g dwt.

Coherence of Midge EC20 Range with Aggregate Toxicity Data

Figure 1 shows a summary of all available toxicity data for solid-phase toxicity testing of sandy sediments from the Ashland site (in the absence of UV light), combining data from SEH (1998), SEH (2001), and URS (2006). Also shown are WDNR TEC, MEC, and PEC effect endpoints, the EPA ESB value, and the range of midge EC20 estimates listed in Table 1. As can be seen, the midge EC20 range lies in an area that is consistent with the distribution of toxic and non-toxic samples; that is, most of the toxic samples lie to the right of this range, and most of the non-toxic samples lie to the left. Also obvious is the very limited about of data in the 600 to $6000~\mu g/g$ range discussed earlier in the document. Finally, the midge EC20 range is consistent with midrange of the WDNR guidance values.

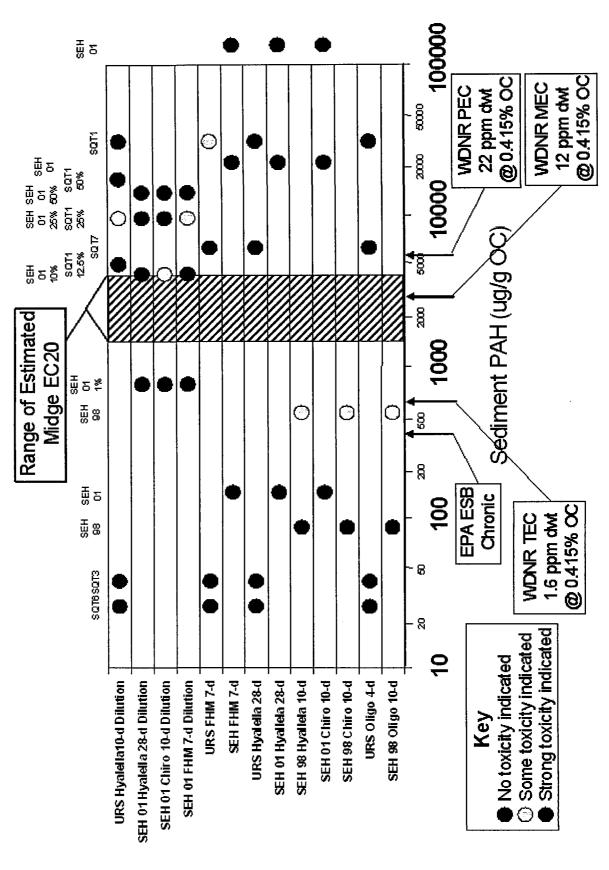
Summary: The range of estimated midge EC20 values is consistent with the distribution of site data and external chemical benchmarks.

Influence of UV Light on PAH Toxicity

The discussion above focuses solely on the effects of site PAHs in the absence of UV. As demonstrated experimentally in studies supporting the BERA, additional toxicity of PAHs can occur when UV light is present. Quantification of these effects, and adjustments to the RAO that may be needed for sediments in shallow water are discussed in a separate memo I forwarded to you previously.

Summary: Effect thresholds discussed in this memo do not include consideration of UV-induced effects, which are discussed in a separate document.

Figure 1 - Summary of Toxicity Data for Sandy Sediments



ATTACHMENT A

ESTIMATION OF MIDGE EC20 VALUES

Because Xcel/URS were unsuccessful at completing toxicity tests with *Chironomus* during the most recent investigations, the only site-specific testing with *Chironomus* across a concentration gradient in sandy sediments was the SEH(2001) dilution study. Regression analysis of these data yielded an EC20 of 4100 μ g/g OC. Because of subtle differences in the slopes of the regression line, the estimated LC20 for this study was actually slightly lower, 3760 μ g PAH/g OC. Because of this, the mean of these two, 3930 μ g PAH/g OC is proposed as the 20% effect level for this study. An uncertainty with this value lies with the analytical characterization which contains some irregularities as pointed out previously by Xcel/URS.

As described in the main body of this document, the water-only fluoranthene data of Schuler et al. (2004) can also be used to estimate sediment effect concentrations. The reported water-only 10-d LC50 for *Chironomus* was 36 μ g/L which, give the Kow and molecular weight of fluoranthene, corresponds to a predicted sediment LC50 of 3280 μ g PAH/g OC. However, this value needs to be corrected from an LC50 to a 20% effect level. An estimate of this correction is available from the exposure response curve from the SEH(2001) sandy sediment dilution study, in which the ratio of the LC50 to the LC20, which is 6090/3760 or 1.62. Because the LC20 and EC20 were so close in this study, the lethality data were not adjusted downward further for sublethal effects. The results in an estimated LC20 based on the Schuler study of 2020 μ g PAH/g OC.

Another point of reference is the toxicity of SQT7 to *Hyalella azteca*; this sediment caused about 80% mortality of *Hyalella* at 6080 μ g PAH/g OC. Toxicity testing of this sediment with *Chironomus* was unsuccessful. However, assuming this concentration in this sediment represents an LC80 exposure for *Hyalella*, other data can be used to estimate a response that might be expected from *Chironomus*. One way is to look at the ratio of the *Hyalella* LC80 in the SEH (2001) sandy sediment dilution test to the *Chironomus* effect threshold mentioned above. This would be a ratio of 17800/3930 or 4.53. Dividing the PAH concentration in SQT7 by this value yields 6080/4.53 or 1342 μ g PAH/g OC. Another way would be to adjust from a *Hyalella* LC80 to a *Hyallela* LC50 using the ratios of those values from the SEH (1.24) and URS (1.34; geo mean = 1.29), adjust to a *Chironomus* LC50 based on the ratio from Schuler (59/36 = 1.64) and to a *Chironomus* LC20 based on SEH(2001) as above (1.62). This gives an estimated *Chironomus* LC20 of 6080/(1.29*1.64*1.62) = 1770 μ g PAH/g OC.

A final method would be to estimate the *Chironomus* LC20 based on the URS(2006) sandy sediment dilution test with *Hyalella*, which gave a 10-d LC50 of 12700 μ g PAH/g OC. This can be adjusted to an estimated *Chironomus* 10-d LC50 using the Schuler data (110/36 = 3.06) and to an LC20 based on SEH (2001;1.62). This yields an estimated *Chironomus* 10-d LC20 of 12700/(3.06*1.62) = 2560 μ g PAH/g OC.

Technical Memorandum on the Derivation of Sediment Preliminary Remediation Goal (PRG) for the Ashland Lakefront Site

INTRODUCTION

The United States Environmental Agency (USEPA) and State of Wisconsin, Department of Natural Resources (DNR) have received and reviewed the second revised Remedial Investigation Report (RI Report) for the Ashland/Northern States Power Lakefront Superfund Site (Site) submitted by Northern States Power Company, a Wisconsin Corporation, a wholly owned subsidiary of Xcel Energy, Inc. (NSPW), pursuant to the Administrative Order of Consent (AOC) (V-W-04-C-764); between NSPW and the USEPA. The RI Report included a Baseline Ecological Risk Assessment (BERA) Report and a Remedial Action Objectives (RAO) Technical Memorandum, which proposes a sediment preliminary remediation goal (PRG) based on the conclusions of the BERA. For the reasons discussed in this Technical Memorandum and pursuant to Section X, (EPA Approval of Plans and Other Submissions), Subparagraph 21(c), of the AOC, USEPA hereby is modifying the RAO Technical Memorandum by incorporating the PRG contained herein. NSPW has 21 days to incorporate the PRG contained herein and resubmit the RAO Technical Memorandum based on EPA's modifications.

Previous BERAs were prepared for the Site by SEH under contract with DNR. SEH completed a BERA of the contaminated sediments adjacent to Kreher Park in 1998 (SEH, 1998). A supplemental BERA was performed in 2001 (SEH 2002), during which additional sediment toxicity testing was conducted to provide information describing the likelihood, nature, and severity of adverse effects to ecological receptors resulting from their exposure to contaminants at the Site. The NSPW iteration of the BERA was conducted to fill data gaps delineated through a data gap analysis of the earlier BERAs as requested by Xcel, and supplements the two other BERAs that have been conducted for this Site. The lack of data (i.e., data gap) in the 3 mg/kg to 300 mg/kg total polycyclic aromatic hydrocarbon (PAH) range of concentrations was to be filled during the NSPW iteration. After reviewing the NSPW BERA (revision 02), the USEPA has concluded that much of the past data collected during the 1998 and 2002 iterations of the BERA were not used to derive the conclusions presented in the NSPW BERA, which was required by the AOC.

This Technical Memorandum looks at the all of the data collected over the three iterations of sediment investigations, and following the sediment quality "triad" approach derives a range of concentrations of PAHs that would be expected to affect the benthic macroinvertebrate community. In addition, this Technical Memorandum draws upon the considerable body of information on PAH toxicity to benthic organisms to supplement the site data. From this range of contaminant concentrations and the expected effects to the benthic communities, USEPA proposes a preliminary remediation goal (PRG) for the sediment portion of the site that will be included in the RAO Technical Memorandum.

This Technical Memorandum does not constitute WDNR's and USEPA's complete comments to the submitted BERA (revision 02), but rather a streamlined approach to arriving at a PRG in order to keep the RI/FS process moving forward. The USEPA's comments to the BERA will be forwarded in a separate letter. These comments will be based on the NSPW's approved Work Plan and the USEPA letter dated September 1, 2006, commenting on the first BERA submittal, as well as subsequent meetings and response letter.

Following the sediment quality triad approach, the subsequent subsections describe the three measures of exposure used to evaluate sediment toxicity:

- 1) Evaluation of sediment chemistry;
- 2) Evaluation of site-specific toxicity tests; and
- 3) Evaluation of site-specific community studies.

Next, a range of PRGs is evaluated with the overall goal being protection of the survival, growth, and reproduction of benthic invertebrate communities. The PRGs produced in this document were derived from data collected through all iterations of sediment investigation at the Site and is based on USEPA review of all data collected. From these PRGs, a single PRG is proposed which will be used by NSPW to complete the Feasibility Study pursuant to the AOC.

1. <u>Sediment Contaminant Chemistry</u>

The sediment investigation conducted at the Site in 1996, and several subsequent investigations, identified the presence of extensive contamination, extending out to 700 feet offshore. Contaminants identified in the sediments include non-aqueous phase tars and oils, PAHs, petroleum volatile organic compounds, heterocyclic aromatic hydrocarbons, phenolic compounds and heavy metals.

The Supplemental BERA report (SEH, 2002) provided a summary of the various contaminants identified and a range of responses associated with the various levels of contamination. Ecological impacts were identified as likely being associated with a variety of the contaminants present. However, the BERA focused on PAHs since they appear to be present in the highest concentrations, are co-located with other contaminants, and appear to demonstrate a response effect.

The 2005 study conducted by URS on behalf of NSPW was intended to supplement the SEH 2002 study by addressing uncertainties related to the range of total PAH (TPAH) concentrations. Sediment Quality Triad (SQT) stations were to be distributed across TPAH concentrations from approximately 2,000 ug/kg to 300,000 ug/kg TPAH (dry weight, dwt), to represent a range of concentrations that encompasses those concentrations where potential ecological effects were likely to be found. At each SQT location, chemical analysis appears to have been conducted for a composite grab sample; each of five replicate samples used for the benthic community study; and a laboratory

homogenized sample utilized for bioassay toxicity tests. Particle size analysis was also conducted for the replicate samples.

Attachment 1 provides a summary of the TPAH, total organic carbon (TOC), and particle size data reported for the 2005 samples. The new data does supplement the 2002 BERA study in that it provides data on the variation at replicates sampling locations. Additionally, the supplemental data for new reference sites provides further information related to background levels.

At many of the sampling sites, calculation of the mean, median, and standard deviation reveals large variation among TPAH concentration in the replicates. At SQT1, SQT7, and SQT8, the standard deviation exceeded the mean and the median. It is apparent the TPAH concentration data are widely dispersed at these locations and that the mean is a poor representation of the data set. For example, at SQT1 the TPAH concentrations among replicates varied over two orders of magnitude, ranging from 12,994 mg/kg to 1,162,300 mg/kg. This variation in data reinforces the need to apply a conservative approach in the interpretation of sediment chemistry results to minimize the potential for underestimating effects at each SQT location.

Background reference site locations are useful for establishing a potential lower boundary for the sediment PRGs, as it is not typically reasonable to set cleanup objectives lower than background concentrations. As shown on Attachment 1, the TPAH concentrations at the reference sand (composite grab samples, homogenized samples and replicate results) were very similar to the 1998 reference sand site location, where the TPAH concentration was 500 ug/kg dwt @ 0.46% OC).

2. <u>Site-Specific Sediment Toxicity Bioassays</u>

Sediment toxicity bioassays conducted in 1998 and 2001 were summarized in the SEH (2002) BERA Supplement. Toxicity tests were conducted for a wide range of TPAH exposures ranging from 424 ug/kg to 836,300 ug/kg TPAH (dwt). Results of the tests indicated that acute (lethal) impacts were always demonstrated above the WDNR draft TPAH probable effect concentration (PEC) of 22,800 ug/kg (at 1% TOC). At concentrations below the WDNR draft TPAH threshold effect concentration (TEC) of 1,610 ug/kg (at 1% TOC), acute impacts were demonstrated only when toxicity tests were conducted with UV exposures. At concentrations between the TEC and PEC, a variety of lethal and sublethal impacts were observed.

The 2005 bioassay study conducted by URS was intended to supplement the SEH studies by addressing uncertainties related to the range of TPAH contaminant concentrations and by including several toxicity tests for both sand and wood substrates.

Attachment 2 includes a "stoplight diagram" that summarize the 1998, 2002, and recent URS study results for the sediment bioassay toxicity tests for sandy sediments. The diagram does not include the results of bioassays conducted with woody sediment, elutriate or UV light exposures. Discussions with Xcel/URS have indicated their interest

in establishing RAOs based on dry weight normalized PAH concentrations in sandy sediments and applying that same value as the RAO for woody sediments.

USEPA evaluation of the toxicity tests conducted with UV light exposures are provided in Attachment 3. The evaluation provides an analysis of expected photo-activated lethal effects expected to be associated with various TPAH concentrations (normalized to 0.41 % OC in sand) and UV exposures related to variable depths within the water column. The evaluation presents survival response curves illustrating sediment toxicity with and without UV exposures. A survival response curve integrating both the URS 2006 results and SEH 2001 results illustrates that a close relationship exists between the test results.

3. <u>Site-Specific Sediment Macroinvertebrate Surveys</u>

The benthic macroinvertebrate community investigation presented in the 1998 BERA (SEH, 1998) indicated that community degradation correlated to sediment TPAH contamination. Subsequent statistical evaluations of the 1998 data by both the WDNR and Dames & Moore in 1999 (excerpts included in Attachment 4 indicated strong correlation between sediment TPAH concentrations and several benthic community metrics, although it was acknowledged the data set was small and the range of contaminant concentrations was limited. The 2005 study conducted by URS was intended, in part, to supplement the 1998 study to address uncertainties related to sample size and range of contaminant concentrations.

According to the EPA's Guidance Manual to Support the Assessment of Contaminated Sediments in Freshwater Ecosystems – Volume III – Interpretation of the Results of Sediment Quality Investigations (EPA-905-BO2-001C, December 2002), "the information on benthic community structure can not be used alone to evaluate the cause of any impacts observed. While such communities certainly respond to chemical contamination in the sediment they are also affected by a wide range of physical factors that are not directly related to sediment quality (e.g., low dissolved oxygen levels, grain size differences, nutritional quality of substrates and water depth). In addition, benthic community composition exhibits significant spatial, short term temporal, and seasonal variability." Thus, if a study encounters a large degree of variability such that discriminatory power is greatly decreased, then the strength of the benthic community study as a line of evidence is decreased commensurately. It appears that there was tremendous variability and resultant uncertainty associated with both the site samples and reference samples collected in the URS 2005 benthic macroinvertebrate community investigation.

Issues associated with the variability and the uncertainty of the 2005 sampling sites used in the statistical evaluation of benthic community impacts include but are not limited to:

- The range of TPAH concentrations for SQT1 replicate samples overlapped the range of TPAH concentrations of most other SQT replicate samples;

- The standard deviation of the dataset exceeds the mean values for TPAH concentrations for replicate samples SQT1, SQT7, SQT8 and reference wood site SQT11;
- The standard deviation of the dataset exceeds the mean value for TOC concentration for reference wood site SQT9;
- The percentage of fine sands is higher in 80% of the reference samples than in 100% of site samples;
- The percentage of fines + fine sands is higher in 80% of the reference samples than in 75% of the site samples;
- The reference sand sites SQT10 and SQT12 exhibited "a strong odor of decaying organic matter" and "elevated levels of ammonia";
- The reference sand sites SQT10 and SQT12 exhibited <50% survival for *Hyalella* azteca 28 day sediment exposure toxicity test;
- The reference wood site SQT11 had no survival in several replicates of the *Lumbriculus* bioaccumulation study;
- The reference sand sites SQT13 and SQT 14 were collected in Fall 2005 versus Spring 2005, more than 3 months after the initial sample collection. Use of this data is questionable for comparison of population metrics due to expected seasonal variation in larval and emergent species; and
- Only three site locations appear to be "sand" sites, and none of the reference sand sites appear to be appropriate. Thus, the sample size for sand sediments does not appear meet the power requirements outlined in the RI/FS workplan.

The statistical analysis presented in the BERA appears to have included benthic community data without "clear and transparent" discussion of how the aforementioned issues were addressed. Input of questionable information into a statistical model produces questionable results and yields low power. If the benthic community study has low power, then it is prone to underestimating effects and is in fact a weak line of evidence rather than a strong one.

It is also noted that the 2005 study neglected to evaluate metrics that appeared to have statistical significance in the 1998 study including midge/oligochaete ratios and midge taxa richness (although this metric was listed in the RI/FS workplan).

Unfortunately, the 2005 benthic community study analysis, as presented in the BERA documentation, provides little value in supplementing the 1998 study and it does not lend value to the current discussion of PRGs.

4. <u>Sediment Quality Triad Integration to Develop a Preliminary</u> <u>Remediation Goal</u>

The accumulated data for sediment chemistry, bioassay toxicity tests, and benthic macroinvertebrate community surveys at this site continue to indicate that it is reasonable to conclude ecological impact is highly likely and contaminant-induced degradation of sediment-dwelling organisms is evident. Several approaches have been evaluated to calculate a site-specific PRG for the sediment TPAH concentrations. The alternate PRGs are presented below in order of ascending concentrations.

- 1) The 2002 Supplemental ERA calculated a PRG of 274 ug TPAH/kg dwt for sandy sediments based on the mean of the no observed effect concentration (NOEC) and the lowest observed effect concentration (LOEC) related to the sediment elutriate dilution series for fathead minnows. USEPA is uncertain if the sediment elutriate dilution series may have overestimated aquatic exposures and effects.
- 2) The toxicity test conducted in 1998 with the contaminated sand sample (616 ug TPAH/g OC or 1,539 ug TPAH/kg dry weight (dwt) @ 0.25% TOC) resulted in sublethal effects for the midge toxicity test. Lethal effects were also documented with this sample with fathead sediment elutriate exposures, lethal effects with Daphnia magna sediment elutriate exposures (coupled with UV), and lethal effects associated with the Lumbriculus variegates sediment exposures (coupled with UV). Using the 1998 contaminated sand sample as the "low observed effects" sample and 1998 reference sand sample (109 ug TPAH/g OC or 500 ug/kg @ 0.46% TOC) as the "no observed effects" sample yields a mean value of 362 ug TPAH/g OC (1,020 ug/kg @ 0.36% TOC).
- 3) Attachment 5 includes a discussion by David Mount (USEPA) related to PAH toxicity thresholds for the site sediments. The document discusses the various impacts that may be associated with a range of sediment TPAH concentrations. The lowest value discussed is **1,340 ug TPAH/g OC** (5,570 ug TPAH/kg dwt @ 0.415% TOC). The discussion of UV toxicity included in Attachment 3 appears to indicate this value would also provide protection from photoactivated toxicity effects for 80% of *Hyallela azteca* in water depths ranging from 2 to 8 feet (with no debris cover). It is noted that this concentration may not address potential sublethal effects.
- 4) The discussion by Dave Mount (Attachment 5) also indicates that the remediation goal of **5,310 ug TPAH/g OC** (22,000 ug TPAH/kg dwt @ 0.415% TOC) recommended by URS in the 2007 BERA is likely to result in substantial acute toxicity to *Hyalella*, *Lumbriculus*, and *Chironomus* species.
- 5) Based on a variety of data sources, the EC20 for midge is expected to lie within a range of 1340 to 3930 ug PAH/g OC (Attachment 5). At an OC of 0.415%, this corresponds to 5.6 to 16.3 ug PAH/g dwt. Use of the EC20 is consistent with the

data quality objective (DQO) for sediment bioassays which states: "If control survival is = 80%, and the difference between Site survival or growth and reference station survival or growth is = 20% (statistically significant difference at a= 0.1) it is indicative of unacceptable risks" (25 January 2005 BERA, Appendix G, Table 4. Data Quality Objectives for 28 day *Hyalella azteca* (Amphipod) with and without UV Light and 20-day *Chironomus dilutus* (formerly *C. tentans*) (*Midge*) *Sediment* Bioassay). The proposed PRG for sediment is 2,295 ug PAH/g OC (9.5 ug PAH/g dwt at 0.415% OC), which is the geometric mean of the above range.

SUMMARY AND CONCLUSIONS

The sediment chemistry and toxicity data presented in the NSPW BERA support the 1998 and 2002 SEH BERA data. The "high weight of evidence" that NSPW attempts to place on the benthic macroinvertebrate community study is not supported by USEPA guidance or the community study data and has little support from the 1998 BERA study. With the variability and uncertainty outlined above, the statistical analysis of the community data is questionable; as such, it was not used to derive the proposed PRG.

The NSPW sediment chemistry data supports earlier chemistry data. The NSPW toxicity testing supports the 1998 and 2001 SEH data sets and supports the PRGs previously proposed in these documents. The UV results from the 2005 study also support the earlier work. In addition, the bioassay data is in agreement with the body of data available in the literature on concentrations of TPAHs that produce toxic effects on benthic communities. Thus, both the chemistry data and the toxicity data are used to support the determination of a PRG for the Site.

In conclusion, the proposed PRG [2,295 ug PAH/g OC (9.5 ug PAH/g dwt at 0.415% OC)] is based on a best professional evaluation of sediment chemistry, bioassay, and benthic community study data collected by SEH and NSPW and conclusions reached by NSPW. This PRG does not include the added effects of UV and is based on a water depth of 6 feet or more. If the final depth of sediments will be less than 6 feet, the PRG for any active remedial intervention will be adjusted downward as based upon UV extinction coefficients measured in Site waters. The adjusted PRGs (assuming no debris cover) are provided in Table 1 of Attachment 3.

Since the RI/FS Work Plan was approved by USEPA, a number of correspondence and meetings have taken place in an attempt to come to a mutually agreed upon PRG for sediment contamination at the Site. A number of differences in application of the data have continued to interfere with this pursuit. In order to keep on schedule for completion of the Feasibility Study, the USEPA has produced this Technical Memorandum. Pursuant to the AOC, NSPW will complete the ordered Feasibility Study using the PRG contained in this Technical Memorandum.

List of Attachments

- 1 Sediment Chemistry Data from URS 2005 BERA
- 2a Summary of Results for Sandy Sediments
- 2b Summary of Results for Woody Sediments
- 3 20 January 2007 Memorandum on "Analysis of Photoactivation Issue Relative to Ashland BERA"
- 4 Excerpts from WDNR and Dames & Moore (1999)
- March 26, 2007 Memorandum on "Discussion of PAH Toxicity Thresholds for Ashland Site Sediments"